[Reprinted from the Journal of Physical Chemistry, 70, 2919 (1966).]

The Reaction of Isopropylbenzene on γ-Irradiated Silica Gels

by Enrique A. Rojo and Robert R. Hentz

Department of Chemistry and the Radiation Laboratory,[1] University of Notre Dame, Notre Dame, Indiana 46556
(Received March 9, 1966)

Dealkylation of isopropylbenzene was studied on three γ-irradiated silica gels. Little or no visible coloration occurs in these solids on irradiation at 37° to doses of 4×10^{21} ev g^{-1}. The yield of benzene initially increases linearly with dose to the solid but approaches a limiting value at large doses; for one of the solids, limiting yields were 2.6 and 15.5 in units of 10^{17} molecules (g of solid)$^{-1}$ at 37 and −196°, respectively. Initial slopes correspond to $G_0(C_6H_6) = 0.067$ at 37° and $G_0(C_6H_6) = 4$ at −196°; the latter value suggests a trapping efficiency for free charge carriers of near 100%. Room-temperature annealing of solid irradiated to saturation at −196° gives a limiting yield identical with that attained in a 37° irradiation. Therefore, the 37° limiting yield must correspond to essentially complete population of certain solid defects. Room-temperature irradiation of solid irradiated to saturation at −196° reduces the benzene yield at a considerably greater rate (than simple annealing) to the 37° limit; G(loss in benzene yield) ≈ 4. Thus, the −196° limiting yield appears to correspond to a steady-state population of certain defects that are not populated appreciably at 37°. A remarkably good correlation exists between the behavior of benzene yields on irradiated silica gel and the reported behavior of certain trapped-electron color centers associated with specific vacancies in a silica matrix. The over-all results suggest that limiting yields, particularly at −196°, are not governed by aluminum content. Irradiation of isopropylbenzene adsorbed on silica gel also was studied. Results are similar to those obtained previously with a silica–alumina. The results suggest that dealkylation of adsorbed isopropylbenzene occurs under irradiation, $G(C_6H_6) \approx 2$, by direct capture of free charge carriers produced in the solid with an efficiency approximating that for their capture by silica matrix defects at −196°.

Introduction

Studies of the dealkylation of isopropylbenzene on γ-irradiated silica–alumina gels have been reported in a series of papers.[2] These studies suggest that at least a portion of the long-lived dealkylation excitations[3] in irradiated silica–alumina may be associated with visible color centers of the irradiated solid; the latter have been associated rather conclusively with the presence of aluminum as a substitutional impurity in the silica matrix.[4-8] The formation of acid sites on irradiation of silica gel at −196° has been reported by Barter and Wagner.[9] Since inherent acid sites are implicated in the catalytic dealkylation of isopropylbenzene on unirradiated silica–aluminas,[10] a question arises as to the role of such radiation-induced acid sites in the dealkylation reaction on irradiated silica–aluminas. The dealkylation excitations produced on room-temperature irradiation of silica–alumina are stable at room temperature;[2] on the other hand, the acid sites formed by irradiation of silica gel at −196° decay at

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is A.E.C. Document No. COO-38-454.

(2) *Cf.* R. R. Hentz, L. M. Perkey, and R. H. Williams, *J. Phys. Chem.*, **70**, 731 (1966), which includes references to earlier papers in this series.

(3) The general expression "excitations" is used in the absence of definitive evidence for the mechanism of energy storage in the solid. It is considered probable that these long-lived excitations are trapped electrons and/or concomitant positive holes.

(4) For a review of the evidence on irradiated quartz, *cf.* the following papers: A. Halperin and J. E. Ralph, *J. Chem. Phys.*, **39**, 63 (1963); J. H. Mackey, Jr., *ibid.*, **39**, 74 (1963).

(5) E. Lell, *Phys. Chem. Glasses*, **3**, 84 (1962).

(6) H. W. Kohn and E. H. Taylor, *Proc. Intern. Congr. Catalyse, 2e, Paris, 1960*, **2**, 1461 (1961).

(7) S. Lee and P. J. Bray, *Phys. Chem. Glasses*, **3**, 37 (1962).

room temperature with a half-time of 2–3 hr.[9] In order to elucidate further the nature of the radiation-induced excitations effective in isopropylbenzene dealkylation, particularly with regard to the role of aluminum and other impurities, the study of this phenomenon has been extended to high-purity silica gels irradiated at room temperature and at −196°.

Experimental Section

A. Chemicals. Eastman Kodak 1481 isopropylbenzene was used; purification procedures have been described.[2] Three silica gels were used. Most of the work was performed with solid A which had a surface area (measured by nitrogen adsorption) of 384 m^2/g and contained 30 ppm of aluminum (30 μg of aluminum/g of solid). This solid was prepared from an acidic alcoholic solution of tetraethyl orthosilicate that was gelled with an alcoholic ammonium hydroxide solution. The hydrogel was washed with water, dried 20 hr at 110°, and then calcined in air for 10 hr at 540°. Solids B and C were obtained from Dr. H. W. Kohn of the Oak Ridge National Laboratory. Their properties and methods of preparation have been described.[11] Solid B is the silica gel specified to contain 5 ppm of aluminum, and solid C is the ultrapure gel stated to contain no impurities detectable by the spark spectrograph. For both solids B and C a surface area of 600 m^2/g is given.

B. Procedures. The general procedures have been described;[2] a review will be presented of the most pertinent features with emphasis on modifications introduced.

The solids were crushed with a Diamonite mortar and pestle to particle sizes of less than 5 mm in longest dimension. After a pretreatment of several days at 500° in air, samples were weighed into 13-mm o.d. Pyrex tubes and evacuated at 10^{-6} torr and 460° for 18–20 hr. In all experiments, the isopropylbenzene was degassed by the conventional freeze–pump–thaw technique and dried over a fresh sodium surface just prior to introduction to the solid. Traces of moisture were found to cause erratic results.

The Reaction of Isopropylbenzene on Irradiated Silica Gel. In these experiments, 0.25 g of isopropylbenzene was transferred to 1.0 g of the irradiated solid by means of liquid nitrogen on the reaction cell. This amount of liquid relative to solid gave sufficiently rapid diffusion to preclude a competitive consumption of the product benzene,[2] and to minimize loss by thermal decay of the less stable excitations formed in −196° irradiations of the solid, yet gave sufficiently high benzene concentrations for convenient and accurate analysis. After warming to room temperature, the liquid and solid were allowed to remain in contact for a period of 90 min (much longer than really necessary) prior to recovery of the liquid and products. The recovery procedure employed boiling water on the reaction cell and liquid nitrogen on an adjacent trap with collection and measurement of noncondensable gas in the calibrated volume of a modified Saunders–Taylor apparatus; recovery was quantitative in 1 hr.

In those experiments in which the solid was irradiated at −196°, the solid was kept in liquid nitrogen until introduction of the isopropylbenzene and then was allowed to come to room temperature. In annealing experiments, after irradiation at −196°, the solid was maintained at room temperature for the desired length of time prior to introduction of isopropylbenzene by the standard procedure.

Irradiation of Isopropylbenzene Adsorbed on Silica Gel. The procedures used were identical with the foregoing with a few exceptions. The desired weight of isopropylbenzene was transferred to a given weight of solid, and the reaction cell was sealed; at least 2 hr elapsed with the reaction cell at room temperature prior to irradiation. The entire range of composition was studied with special emphasis on low isopropylbenzene concentrations. At the lowest concentrations of isopropylbenzene in the system, product recovery times were extended to 2 hr. As in the earlier studies with silica–alumina,[2] the ratio of dose absorbed by the system to weight of isopropylbenzene present was maintained constant but at the much lower value of 1.4×10^{18} ev/mg of isopropylbenzene.

Irradiations. All samples were irradiated in a 10-kc ^{60}Co source under conditions giving a dose rate of 1.75×10^{18} ev g^{-1} min^{-1} to a Fricke dosimeter solution using $G(Fe^{3+}) = 15.6$. Dose to a particular system was determined by correction for the electron density relative to that of the dosimeter and for decay of the ^{60}Co. Samples initially at room temperature attained a temperature of 37° during irradiation; these will be referred to as room-temperature irradiations. The −196° irradiations were performed with the reaction cell immersed in a dewar of liquid nitrogen. The small change in dose rate under these conditions was shown to be without effect.

Analyses. The liquids were analyzed by vapor phase chromatography on an F and M Model 609 with a

(8) G. K. Boreskov, V. B. Kazanskii, Yu. A. Mishchenko, and G. B. Pariiskii, *Dokl. Akad. Nauk SSSR*, 157, 384 (1964).

(9) C. Barter and C. D. Wagner, *J. Phys. Chem.*, 68, 2381 (1964).

(10) *Cf., e.g.*, A. E. Hirschler, *J. Catalysis*, 2, 428 (1963), and D. Barthomeuf, *Compt. Rend.*, 259, 3520 (1964).

(11) H. W. Kohn, *J. Catalysis*, 2, 208 (1963).

flame-ionization detector. A 2-m column of Apiezon-L on Chromosorb-P was used at 200°.

Results

The Reaction of Isopropylbenzene on Irradiated Silica Gel. On solid A at both irradiation temperatures, 37 and −196°, the yield of benzene initially increases linearly with increased dose to the solid but approaches a limiting value at large doses (*cf.* Figure 1). Only the limiting yields were determined on solids B and C; comparison of the saturation yields is presented in Table I. The initial rates of increase in yield with dose to solid A differ greatly at the two irradiation temperatures; at −196° the initial rate corresponds to $G_0(C_6H_6) = 4$, and at 37° to $G_0(C_6H_6) = 0.067$. (G_0 is the number of molecules formed per 100 ev absorbed by the solid at low dose.) Further, the approximate dose required for attainment of a yield essentially equal to the saturation value is about 16 times greater at 37°. On solid A, the saturation yields of gas (noncondensable at −196°) were 0.22×10^{17} and 0.03×10^{17} molecules/g of solid at irradiation temperatures of −196 and 37°, respectively. No products could be detected in blank experiments on the unirradiated solids.

Table I: Comparison of Benzene Yields[a] in Reaction of Isopropylbenzene on γ-Irradiated Silica Gels

	Solid		
	A	B	C
Al content[b]	6.7	1.1	<0.11
	Benzene yield[b]		
Temp[c] = 37°	2.6	0.10	0.11
Temp[c] = −196°	15.5	0.28	0.31

[a] Yields are saturation values obtained by averaging yields on the plateau reached at large values of dose per gram of solid. [b] Aluminum content and benzene yield are expressed in units of 10^{17} atoms or molecules, respectively, per gram of solid. [c] Irradiation temperature.

A sample of solid A that was irradiated to a saturation dose at 37° was allowed to stand 20 days at room temperature prior to introduction of isopropylbenzene; no decrease in benzene yield was observed. Similarly, a sample of solid A irradiated at −196° showed no decay of activity after 24 hr at −196°. However, when the solid is irradiated at −196° and then allowed to warm up and stand at room temperature for some period prior to introduction of isopropylbenzene, the results are quite interesting (anneal time is measured as the interval between the removal of liquid nitrogen after irradiation of the solid at −196° and the replacement of liquid nitrogen for introduction of isopropylbenzene).

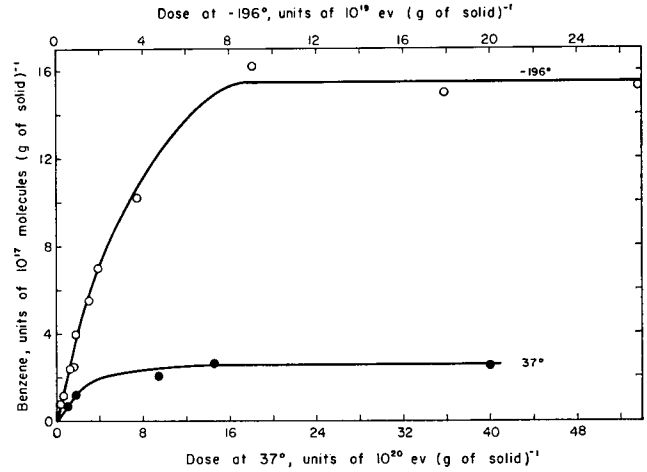

Figure 1. Benzene yields in reaction of isopropylbenzene on γ-irradiated silica gel A.

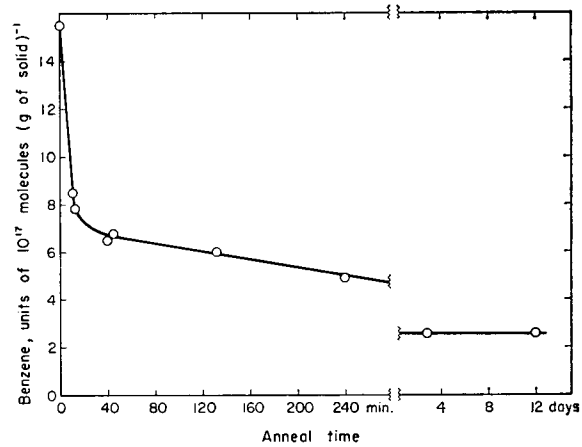

Figure 2. Benzene yields after annealing at room temperature of silica gel A irradiated to saturation at −196°.

On irradiation of solid A to a saturation dose at −196°, the yield of benzene is halved after an anneal time of only 13 min (*cf.* Figure 2).[12] This relatively rapid decay of the activity, of a sample irradiated to saturation at −196°, is followed by a much slower decay; after an anneal time of 68 hr, the benzene yield has fallen to a value equal to the saturation yield obtained in a 37° irradiation. No further decrease was observed in a sample irradiated at −196° and stored 12 days at room temperature. Thus, the limiting yield attained

(12) When isopropylbenzene is introduced to solid irradiated at −196° without prior warm-up (zero anneal time), it seems probable that some decay of activity would occur before complete diffusion and reaction of the isopropylbenzene as the system is allowed to warm up. Thus, all zero anneal time yields are lower limits; such yields are quite reproducible.

by room-temperature annealing of solid irradiated at −196° is identical with the limiting yield attained in a room-temperature irradiation. Such annealing behavior was observed for all samples of solid A irradiated at −196° to a dose sufficient to give a benzene yield in excess of 2.6×10^{17} molecules/g of solid, the saturation yield in 37° irradiations. In −196° irradiations of solid A to doses corresponding to benzene yields less than 2.6×10^{17} molecules/g of solid, no decay was observed for anneal times up to 20 days.

In a series of experiments, the results of which are presented in Table II, solid A first was irradiated to a saturation dose at −196°. About 3 min after removal from liquid nitrogen, the solid again was irradiated (at near room temperature) for the time specified in Table II; it then was allowed to stand at room temperature to give the total anneal time, inclusive of the room-temperature irradiation time, between removal from liquid nitrogen after the first irradiation and immersion in liquid nitrogen for introduction of isopropylbenzene. Obviously, rigorous control of all experimental conditions is not possible in such experiments. Nevertheless, the results clearly establish that irradiation at room temperature accelerates the decay of excitations produced by irradiation at −196°. Furthermore, the limiting value of the benzene yield obtained is again the same as that obtained in a 37° irradiation, 2.6×10^{17} molecules/g of solid. Finally, the decrease in benzene yield of $\sim 3 \times 10^{17}$ molecules/g of solid for a dose of 7.6×10^{18} ev g^{-1} (*cf.* Table II) corresponds to $G \approx 4$ for the destruction of excitations, which may be compared to $G_0(C_6H_6) = 4$ in irradiation at −196°. Considering the experimental uncertainties and over-all complexity of the situation in such an irradiated solid, such an exact correspondence of the two G values is probably fortuitous; however, even an approximate correspondence would be very suggestive.

On irradiation of solid A at 37°, no color was observed at doses up to 4×10^{21} ev g^{-1}; a very slight, nonuniform coloration was observed in solids B and C. Beginning a few seconds after removal from liquid nitrogen of solid A irradiated at −196°, a strong green glow was observed that decayed almost completely by the time room temperature was reached; no quantitative observations of the thermoluminescence have been made.

Irradiation of Isopropylbenzene Adsorbed on Silica Gel. The results obtained in irradiation of isopropylbenzene adsorbed on solid A are shown in Figure 3. (G is the number of molecules formed per 100 ev absorbed by the whole system; F is the electron fraction of isopropylbenzene in the system.) The results for both $G(C_6H_6)$ and G(gas) are very similar to those obtained earlier with a silica–alumina (10% by weight of alumina);[13] *e.g.*, in the earlier work, $G(C_6H_6)$ reached a maximum of 1.45 at $F = 0.0018$, and $G(H_2)$ reached a maximum of 0.21 at $F = 0.007$ and then passed through a minimum at $F \approx 0.15$, in the neighborhood of complete surface coverage. The passage of $G(H_2)$ through a minimum at $F \approx 0.15$ was more evident in results obtained on another silica–alumina, for which the maximum $G(H_2) = 0.28$ occurred at $F = 0.0046$.[14] The lower values of $G(C_6H_6)$ obtained in the earlier work are attributable to the use of a dose about 20 times larger in that work than in the present study; irradiation of isopropylbenzene adsorbed on solid A to the same large dose at $F = 0.007$ gave $G(C_6H_6) = 1.01$

Table II: The Effect of Irradiation During Room Temperature Annealing of Solids Initially Irradiated[a] at −196°

Anneal[b] time, min	Irradiation[c] time, min	Benzene[d] yield
11	...	8.5
11	5	5.4
13	...	7.8
13	7	4.0
40	...	6.5
40	18	2.6

[a] Initial irradiations at −196° were to a sufficiently large dose to ensure attainment of saturation. [b] Total time between removal of liquid nitrogen after the initial irradiation and its replacement prior to introduction of isopropylbenzene (includes room-temperature irradiation time). [c] Room-temperature irradiation time at a dose rate to the solid of 1.51×10^{18} ev g^{-1} min^{-1}. [d] Units of 10^{17} molecules per gram of solid.

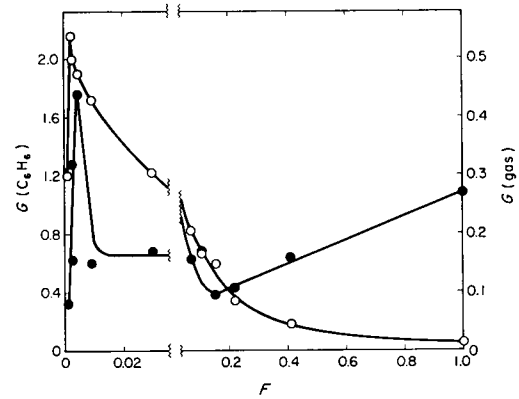

Figure 3. Yields in irradiation of isopropylbenzene adsorbed on silica gel A: O, C_6H_6; ●, gas volatile at −196°. F is the electron fraction of isopropylbenzene in the system.

(13) R. R. Hentz, *J. Phys. Chem.*, 66, 1625 (1962).
(14) R. R. Hentz, *ibid.*, 68, 2889 (1964).

which may be compared with $G(C_6H_6) = 1.05$ obtained at $F = 0.007$ for the silica–alumina.[13] At the lower doses used in this work, decomposition of isopropylbenzene was of the order of 1%.

Discussion

A. The Reaction of Isopropylbenzene on Irradiated Silica Gel. In quartzes and silica-base glasses and gels, the mechanism of formation and the nature and interrelationships of the many color centers formed by high-energy radiation are not thoroughly understood.[4,5,15–18] Consequently, it would be premature to attempt the development of a unique and integrated interpretation of the chemical effects occurrent on interaction of isopropylbenzene and other substances with irradiated silica and silica–alumina gels. Nevertheless, certain color centers in silica-base solids have been rather thoroughly studied, and their behavior and nature have been established with reasonable certainty. By comparison of the behavior of such color centers with that of the isopropylbenzene dealkylation reaction on irradiated silica and silica–alumina gels, a strong correlation is established between these color centers and the excitations effective in dealkylation.

The Role of Impurities. The results in Table I are to be compared with benzene yields of 13–233 × 10^{17} molecules/g of solid obtained on silica–aluminas irradiated at room temperature to a saturation dose;[2,14] these silica–aluminas contained ~1.2 × 10^{21} atoms of Al/g of solid. For the room temperature irradiations, a qualitative correlation is observed between the yield of benzene and the aluminum or total impurity content.[19] Similar qualitative correlations have been reported between the aluminum content of irradiated silica gels and their visible color, H_2–D_2 exchange activity, and irreversible H_2 adsorption.[8,11] Nevertheless, the relationship between benzene yield and impurity content is quite evidently not a proportional one; certainly the aluminum content does not govern the limiting yield. Similarly, poor quantitative correlations have been obtained between aluminum content and the visible color of irradiated quartz and silica; this has been accounted for as owing to presence of part of the aluminum in interstitial sites,[20] rather than in substitutional sites where aluminum acts as a positive-hole trap and gives rise to the visible color[21] and a characteristic esr signal.[22] Such an explanation cannot account for the low benzene yields relative to aluminum content on the silica–aluminas for which a major fraction of the benzene yield has been associated with the visible color centers;[2] in such solids, the aluminum appears to be largely substitutional.[23] The benzene yield on silica–alumina may be limited by the availability of stable electron traps or of specific charge-compensation ions essential to stabilization of positive holes on substitutional aluminum.[4,5]

Although the aluminum content of the three silica gels is sufficient to account for the yields of benzene in room-temperature irradiation, the absence of significant visible coloration in the irradiated solids suggests that the traces of aluminum are not substitutional in these solids. On solids A and C irradiated at −196°, benzene yields actually exceed the aluminum content. One might argue that benzene yields on the irradiated silica gels are related to total impurity content, which may exceed the benzene yield even in the case of solid A irradiated at −196°. In the ensuing discussion, remarkably good correlations are established between the behavior of benzene yields on irradiated solid A and that of certain color centers, namely the E′ centers (trapped electrons) absorbing at ~0.22 μ, associated with specific vacancies in the silica matrix. It is our opionion that limiting benzene yields on the three silica gels are governed by the availability of defects inherent in the silica matrix and not by cationic impurities. The difference between the benzene yield on solid A and those on solids B and C may be attributable to the effect of the very different methods of preparation on the concentration of silica matrix defects produced; *e.g.*, it has been observed that anion impurities, particularly OH^-, may occupy oxygen vacancies and preclude formation of E′ centers on irradiation.[18] Solids B and C were prepared with $SiCl_4$ while the solid A preparation used ethyl silicate. Although the large difference in surface area of solid A as compared to solids B and C reflects an effect of preparation method on structure, it is evident that benzene yields are not directly related to surface area. It should be noted that an appreciable fraction of the benzene yield on irradiated silica–alumina was shown not to be associated with visible color centers;[2] it is probable that this yield of benzene arises from the same centers that are effective in the silica gels.

(15) *Cf.* the ten papers from the Mellon Institute Symposium on Defect Structure of Quartz and Glassy Silica, *J. Phys. Chem. Solids*, **13**, 271 (1960).

(16) W. D. Compton and G. W. Arnold, Jr., *Discussions Faraday Soc.*, **31**, 130 (1961).

(17) C. M. Nelson and R. A. Weeks, *J. Appl. Phys.*, **32**, 883 (1961).

(18) R. A. Weeks and E. Lell, *ibid.*, **35**, 1932 (1964).

(19) Other impurities—such as iron, magnesium, copper, calcium, and sodium—were present in silica gels A and B at about the same level as the aluminum.

(20) A. J. Cohen, *J. Phys. Chem. Solids*, **13**, 321 (1960).

(21) R. W. Ditchburn, E. W. J. Mitchell, E. G. S. Paige, J. F. Custers, H. B. Dyer, and C. D. Clark, Bristol Conference on Defects in Crystalline Solids, The Physical Society, London, 1955, p 92.

(22) M. C. M. O'Brien and M. H. L. Pryce, ref 21, p 88.

(23) A. Leonard, S. Suzuki, J. J. Fripiat, and C. DeKimpe, *J. Phys. Chem.*, **68**, 2608 (1964).

Correlations with the E′ Centers. In fused silicas of high purity, in which no visible color is produced by irradiation, certain radiation-induced ultraviolet absorption bands are enhanced by irradiation at −196°.[16,24,25] Arnold and Compton[25] report that on irradiation and measurement at 77°K, the intensity of the 0.215-μ band (an E′ center) was ~10 times greater than the intensity observed after an irradiation at ~300°K and measurement at 77°K. In addition, these authors observed that when the sample irradiated at 77°K is warmed to room temperature and then immediately remeasured at 77° K, the 0.215-μ absorption is reduced to about half its original value. Further loss in the 0.215-μ absorption was observed to occur slowly at room temperature and to approach the value obtained when the irradiation was made at room temperature. The parallel between these results and the benzene yield results is striking (*cf.* Figures 1 and 2).

The same limiting yield of benzene is attained in room-temperature irradiation as in the decay at room temperature of centers produced by a saturation dose at −196°; therefore, this limiting yield of benzene at room temperature must correspond to essentially complete population of certain silica matrix defects, rather than to attainment of a radiation-induced steady-state population of such defects. Furthermore, the annealing behavior suggests a quantitative conversion of centers formed on irradiation at −196° into available room-temperature centers on warming. Again, a similar interconversion of electron-type centers has been observed in optical bleaching experiments on irradiated fused silicas;[26-29] *e.g.*, Nelson and Weeks observe that interconversion of E_1' and E_2' centers occurs with only a small loss of total intensity and conclude that it is easier to transfer electrons between electron-type centers than to cause electron-hole recombination at a hole center.

The results of Table II show that centers produced on irradiation at −196° are converted into the room-temperature centers by irradiation at room temperature;[30] the loss in benzene yield due to the room-temperature irradiation corresponds to a $G(-C_6H_6) \approx 4$, which equals $G_0(C_6H_6)$ at −196°. Such a result suggests that the limiting yield of benzene in irradiation at −196° corresponds to a steady-state population of the unstable (at room temperature) centers; these centers must have a negligible cross section for formation at room temperature. The $G_0(C_6H_6) \approx 4$ at −196° corresponds to 25 ev per center, which is about what might be expected for the formation of free charge carriers in silica. Thus, at −196° a high capture efficiency for the free charge carriers is indicated; that for formation of the room-temperature centers is ~60-fold smaller.

Correlation with Other Chemical Effects on Irradiated Silica Gels. The dealkylation of isopropylbenzene appears to occur on a variety of color centers produced by irradiation of silica and silica–alumina gels. The centers effective in dealkylation that are produced by irradiation of silica gel at −196° seem to correspond to the acid centers of Barter and Wagner.[9] These authors observed no coloration of their irradiated silica gel and observed decay of the radiation-induced acid centers at room temperature. We suggest that such centers are associated with some kind of color center characteristic of the silica matrix. In addition, there are radiation-induced dealkylation centers in silica gel and in silica–alumina that are stable at room temperature and also do not absorb in the visible and, hence, are not associated with positive holes trapped on substitutional aluminum impurity. Such are the centers formed at room temperature in solid A and those which remain after a hydrogen or thermal bleach of visible color centers in silica–alumina.[2] These centers, to which −196° centers convert on warming of a −196° irradiated silica, also appear to be related to defects inherent in the silica matrix. Finally, in silica–alumina[2] dealkylation of isopropylbenzene has been shown to occur also on the visible color centers (stable at room temperature) identified as positive holes trapped on substitutional aluminum. Boreskov, *et al.*,[8] have demonstrated that in a silica gel that is colored by irradiation, such aluminum centers are responsible for the color, for the irreversible adsorption of hydrogen concomitant with bleaching of the color, and for a major part of the H_2–D_2 exchange activity measured at −196°. It has been noted previously[2] that dealkylation of isopropylbenzene does not occur on the radiation-induced H_2–D_2 exchange sites studied by Kohn and Taylor;[6] these sites do not absorb in the visible (they remain after hydrogen bleaching) and are poisoned by oxygen.

B. Irradiation of Isopropylbenzene Adsorbed on Silica

(24) P. W. Levy, *J. Phys. Chem. Solids*, 13, 287 (1960).

(25) G. W. Arnold and W. D. Compton, *Phys. Rev.*, 116, 802 (1959).

(26) F. S. Dainton and J. Rowbottom, *Trans. Faraday Soc.*, 50, 480 (1954).

(27) C. M. Nelson and R. A. Weeks, *J. Am. Ceram. Soc.*, 43, 396 (1960).

(28) C. M. Nelson and J. H. Crawford, Jr., *J. Phys. Chem. Solids*, 13, 296 (1960).

(29) The existence of such interconversions in the alkali halides has been known for some time; *cf.* K. Przibram, "Irradiation Colours and Luminescence," Pergamon Press Ltd., London, 1956, p 72.

(30) A similar effect has been observed in KCl by H. U. Harten, *Z. Physik*, 126, 619 (1949).

Gel. The results obtained in irradiation of isopropylbenzene adsorbed on silica gel are similar to those obtained earlier on silica–alumina.[13] Such similarity casts doubt on the earlier identification of the occurrence of a maximum in $G(C_6H_6)$ with saturation by added isopropylbenzene of inherent catalytic sites in the solid. Rather, the effects must now be considered as independent of aluminum content and related to some characteristic inherent in the microporous silica-base solids.

A maximum $G(C_6H_6) \approx 2$[31] occurs at low doses per gram of solid corresponding to those for which $G_0(C_6H_6) \approx 4$ in the $-196°$ irradiations of solid without isopropylbenzene. This suggests the possibility that the dealkylation reaction in irradiation of adsorbed isopropylbenzene at room temperature may occur *via* the unstable $-196°$ centers; this would require that the rate of reaction be rapid relative to the rate of radiation-induced destruction of these centers. Such a possibility would also require the rate of formation of unstable $-196°$ centers to be about the same at room temperature as at $-196°$; however, such a requirement cannot be reconciled with the essentially zero steady-state yield of the unstable centers in irradiation of the solid without isopropylbenzene at room temperature. Consequently, we conclude that dealkylation of adsorbed isopropylbenzene occurs under irradiation by direct capture of free charge carriers with an efficiency almost equal to that for their capture by silica matrix defects at $-196°$.

Acknowledgment. The authors are grateful to Socony Mobil Oil Company, Inc., for synthesis and characterization of the silica gel designated as solid A and to Dr. H. W. Kohn of the Oak Ridge National Laboratory for the silica gels designated as solids B and C.

(31) Although the dose per milligram of isopropylbenzene was maintained approximately constant in most of these experiments, the point for $G = 2.0$ in Figure 3 corresponds to a sixfold greater dose. Thus, the four points in Figure 3 in the range $G = 1.72$–2.16, inclusive, cover a range of doses per gram of solid under very similar conditions and give an average $G(C_6H_6) \approx 2$.