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Dealkylation of Isopropylbenzene on γ-Irradiated Silica–Alumina. The Effect of Various Reagents on the Active Centers and on Their Yield

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A silica–alumina gel was exposed to a gaseous reagent during or after γ irradiation, and the yield of benzene (molecules formed per gram of solid) on subsequent exposure to isopropylbenzene was determined. The following reagents were used: N_2, H_2, O_2, CO_2, N_2O, C_2H_4, NH_3, H_2S, CO, and SO_2. In general, effects of the reagents on the benzene yield correlate with previously reported effects of the same reagents (for corresponding conditions) on the positive-hole esr spectrum of the irradiated silica–alumina. The esr spectrum includes contributions from a positive hole trapped on a bridging oxygen atom bonded to a substitutional Al atom and from certain positive holes trapped on nonbridging oxygen. Certain of the results indicate that the yield of benzene from contact of isopropylbenzene with silica–alumina irradiated alone, like the yield of trapped positive holes seen in the esr spectrum, is limited by the number of preexisting electron traps in the silica–alumina matrix. The total results seem to require that electron transfer from isopropylbenzene to a trapped positive hole (of any kind contributing to the esr spectrum) be the primary process in isopropylbenzene dealkylation on γ-irradiated silica–alumina.

Introduction

Irradiation of silica–alumina gel with ^{60}Co γ rays imparts a very dark, essentially black, color to the solid, and subsequent introduction of isopropylbenzene bleaches the solid with concomitant formation of benzene.[2] With increase in radiation dose to the silica–alumina gel, the number of molecules of benzene produced per gram of solid increases to a limiting value designated the plateau yield.[3] Such phenomena are associated not with impurity content but with properties inherent in the structure or composition of the silica–alumina gel that are sensitive to variations in the preparation and pretreatment tech-

(1) The Radiation Laboratory of the University of Notre Dame is operated under contract with the U. S. Atomic Energy Commission. This is AEC Document No. COO-38-827.
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niques[3] and to age of the solid (stored in a closed bottle with atmospheric gases at room temperature).[4] The results suggest that benzene yields are limited by the number of certain preexisting defects in the silica–alumina matrix (*e.g.*, traps for electrons or positive holes) that are populated by γ irradiation.[3,5] Moreover, though exposure of γ-irradiated silica–alumina to oxygen has no effect on either color of the solid or the amount of benzene formed on subsequent exposure to isopropylbenzene, exposure to hydrogen bleaches γ-irradiated silica-alumina and reduces the amount of benzene formed on subsequent exposure to isopropylbenzene.[4] The same reduced yield of benzene is obtained on exposure of thermally bleached γ-irradiated silica–alumina to isopropylbenzene.[4] Thus, the dealkylation of isopropylbenzene is associated with centers that do not absorb in the visible as well as with centers that do.

The esr spectrum of γ-irradiated silica–alumina gel consists of a narrow trapped-electron signal at $g = 2.0010$ and a broad (width of ~44.5 G) positive-hole spectrum at $g = 2.0088$ which includes a partially resolved six-line component with a splitting of 8.5 G.[6] More than one kind of center contributes to the positive-hole esr spectrum. As noted with respect to the almost identical esr spectrum of irradiated aluminosilicate glasses,[7] the six-line component indicates presence of the center observed by Griffiths, *et al.*,[8] in irradiated quartz single crystals and identified by O'Brien and Pryce[8] as a positive hole trapped on a bridging oxygen atom that is bonded to a substitutional Al^- ion. The esr spectrum of this center, designated the Al positive-hole center, is removed by contact of irradiated silica–alumina gel with hydrogen[6] or by thermal annealing of irradiated aluminosilicate glass,[7] and a spectrum remains that is attributed to a positive hole trapped on nonbridging oxygen.[6,7,9]

In an esr study of γ-irradiated silica–alumina gel,[6] behavior of the esr signal of the Al positive-hole center was found, without exception, to parallel behavior of the visible coloration on exposure of the irradiated solid to each of 18 reagents and on irradiation in the presence of each of 12 reagents. Thus, as in irradiated quartz,[8] Al positive holes appear to be the centers that absorb in the visible. Further, results of the esr study indicate that the yield of trapped positive holes is limited by the availability of electron traps and that trapped positive holes can be neutralized by electron transfer from certain reagents (including isopropylbenzene).[10,11] Such results suggest that electron transfer from isopropylbenzene to a trapped positive hole (of any kind contributing to the esr spectrum) is the primary step in isopropylbenzene dealkylation on γ-irradiated silica–alumina gel. Then the yield of benzene, like the yield of trapped positive holes, should be limited by the availability of electron traps.

In the work reported in the present paper, inferences from the previous work[2-6] have been subjected to further test. Silica–alumina gel has been exposed during or after γ irradiation to ten of the reagents used in the esr study,[6] and the yield of benzene on subsequent exposure to isopropylbenzene has been determined. Effects of the reagents on the dealkylation yield and the esr spectrum, for corresponding conditions, are compared.

Experimental Section

The silica–alumina used in this work is a conventional catalyst with 10 wt % alumina and a surface area of 400 m^2/g (solid A of a previous publication in which its properties are described[3]). Purification of isopropylbenzene has been described.[12] All gases were obtained from Matheson Co. Gases noncondensable at 77°K were dried by passage through a silica gel column and through traps at 77°K. Condensable gases were passed through a silica gel column and were purified by trap-to-trap distillation at 77°K with the middle fraction being retained for use.

The general procedures, including dosimetry and gas-chromatographic determination of benzene, have been described.[2-6,13] A brief review of the most pertinent features follows. Materials were irradiated at room temperature with a ^{60}Co source. The silica–alumina was first heated for about 20 hr at 500° in air. Then 2 g of the solid in a 13-mm o.d. Pyrex tube with break-seal was evacuated at 10^{-6} Torr and 500° for 18–20 hr. Gaseous reagents were introduced, either before or after irradiation, at a pressure of 150 Torr as in the esr study.[6] Gases added after γ irradiation were kept in contact with the silica–alumina for 1 hr. Prior to introduction of another gas or isopropylbenzene, gas in contact with silica–alumina was removed by pumping the reaction cell on a high-vacuum line for 3–4 hr or until there was no increase in pressure for several minutes after isolation of the reaction cell from the pumping system. Removal of gaseous reagents or their reaction products was not always complete as shown by unusual color changes, in some cases, in subsequent treatment of the silica–alumina with isopropylbenzene and by the odor of NH_3 and SO_2, in experiments with these gases, in the recovered isopropylbenzene. Isopropylbenzene (0.2 g) was degassed by the conventional freeze–pump–thaw technique, dried over a fresh sodium surface, and transferred to the silica–alumina by means of liquid nitrogen on the reaction cell. Isopropylbenzene and silica–alumina remained in contact for 1 hr at room temperature. Then, a boiling-water bath was placed around the reaction cell and isopropylbenzene and products were collected for 1 hr in an adjacent trap at 77°K. Such a procedure gives quantitative recovery of benzene.

Results and Discussion

As observed in previous work, the silica–alumina is darkened by irradiation and with increase in dose the yield of benzene increases to a limiting value, the plateau yield. Table I gives benzene yields obtained from contact of γ-irradiated silica–alumina with isopropylbenzene after exposure of the solid to various reagents during or after irradiation. In all experiments in Table I, the dose exceeded that required ($\sim 1 \times 10^{21}$ eV g^{-1}) to attain the plateau yield of positive holes[6] and benzene. No benzene was ob-

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(9) J. Vedrine, G. Dalmai, C. Naccache, and B. Imelik, *J. Chim. Phys.*, **65**, 2129 (1968), suggest that six positive-hole centers, including the Al center, contribute to the positive-hole esr spectrum of irradiated silica–alumina gel.
(10) Disappearance of visible coloration and the Al positive-hole esr spectrum on exposure of γ-irradiated silica–alumina gel to various reagents is accompanied by a luminescence which has been attributed to neutralization of the Al positive-hole center by an electron donated by the reagent at the solid surface.[11]
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TABLE I: Benzene Yields Obtained from Contact of γ-Irradiated Silica–Alumina with Isopropylbenzene after Exposure of the Solid to Various Reagents during or after Irradiation[a]

Expt no.	Reagent[b] A	Reagent[b] B	Benzene yield[c]
1	..	..	8.6
2	N_2	..	8.5
3	..	N_2	8.7
4	..	H_2	5.3
5	H_2	..	1.5
6	O_2	..	26.0
7[d]	O_2	..	26.0
8	O_2	H_2	5.6
9	CO_2	..	24.8
10	CO_2	H_2	5.1
11	..	CO_2	8.4
12	N_2O	..	27.5
13	..	N_2O	8.6
14	C_2H_4	..	0.0
15[e]	..	C_2H_4	0.0
16	NH_3	..	0.0
17	..	NH_3	0.0
18	H_2S	..	0.0
19	..	H_2S	0.0
20	CO	..	8.6
21	..	CO	7.8
22	SO_2	..	8.8
23	..	SO_2	7.9

[a] In all experiments, the dose exceeded that required ($\sim 1 \times 10^{21}$ eV g^{-1}) to attain the plateau yield of positive holes and of benzene. [b] Reagents were present at 150 Torr; those in column A were present during irradiation and those in column B were introduced after irradiation. [c] Units are 10^{17} molecules of benzene per gram of silica–alumina. [d] After irradiation O_2 was removed and the silica–alumina was again irradiated to a saturation dose before addition of isopropylbenzene. [e] Owing to the large adsorption of C_2H_4, a second portion was required.

tained from contact of unirradiated silica–alumina with isopropylbenzene.

Discussion of the present results is facilitated by use of the following model which was proposed in the esr study[6] for interpretation of results obtained in radiation studies with silica–alumina gel. Radiation generates H atoms, mobile electrons, and mobile positive holes in the silica–alumina. The mobile positive hole may be thought of as an O^- ion the position of which moves through the solid by electron-transfer processes until the hole is trapped at a site of lower energy, *e.g.*, on a bridging oxygen atom bonded to a substitutional Al atom[7,8] or on some kind of nonbridging oxygen atom.[7,9] The Al positive-hole center absorbs in the visible and contributes the six-line component to the positive-hole esr spectrum; certain positive holes trapped on nonbridging oxygen, that do not absorb in the visible, are responsible for the positive-hole esr spectrum left after exposure of irradiated silica–alumina to hydrogen. An equal number of electrons is trapped and most of these are trapped in such a way as to escape detection in the esr spectrum. At room temperature, H atoms react with some kind of defect at which ionization occurs to give the tapped-electron signal at $g = 2.0010$.

The presence of N_2 during irradiation or the introduction of N_2 after irradiation has no effect on the visible coloration or esr spectrum of irradiated silica–alumina.[6] Thus, N_2 does not react with any of the mobile or trapped species. Accordingly, benzene yields in experiments 2 and 3 do not differ significantly from that in experiment 1.

The benzene yield in experiment 4 is substantial but is less than that in experiment 1. Because exposure of irradiated silica–alumina to isopropylbenzene removes the color and the *entire* positive-hole esr spectrum,[6] the result of experiment 4 indicates that benzene formation is associated with both the Al positive-hole centers and those positive holes trapped on nonbridging oxygen that are left after H_2 has neutralized the Al center. Comparison of the benzene yields in experiments 4 and 5 indicates that H_2 present during irradiation intercepts the mobile positive holes that are precursors of the trapped positive holes involved in benzene formation. In accord with such conclusions, irradiation of silica–alumina in the presence of H_2 gives no visible coloration and an ill-defined broad signal of very low intensity in the region of the positive-hole esr spectrum.[6]

The results in experiments 1 and 4 also confirm the earlier observation[4] that radiation-induced dealkylation activity associated with visible coloration decreases with age of the unirradiated silica–alumina while that not associated with visible coloration is not affected. The plateau yield of benzene in experiment 1 is 8.6×10^{17} molecules/g compared with that of 13×10^{17} molecules/g last obtained;[4] however, the yield in experiment 4 of 5.3×10^{17} molecules/g, after exposure of irradiated silica–alumina to H_2, is the same as that last obtained in such an experiment.[4] Consequently, the benzene yield associated with visible coloration is now 3×10^{17} molecules/g, compared with the earlier 8×10^{17} molecules/g, and is now less than the age-independent yield not associated with visible coloration.

The presence of C_2H_4, NH_3, or H_2S during irradiation of silica–alumina or their introduction after irradiation results in elimination of visible coloration and the *entire* positive-hole esr spectrum.[6] Consequently, the absence of detectable benzene formation in experiments 14–19 provides additional support for the identification of benzene formation with all positive-hole centers that contribute to the esr spectrum.

Exposure of irradiated silica–alumina to such effective electron scavengers as O_2, CO_2, or N_2O has no effect on the visible coloration or esr spectrum.[6] Accordingly, dealkylation yields are not affected by prior exposure of the irradiated solid to O_2 (as shown in previous work[4]) or to CO_2 or N_2O (as shown in experiments 11 and 13). However, when silica–alumina is irradiated in the presence of O_2, CO_2, or N_2O, the solid becomes very much darker and height of the positive-hole esr signal is 2–3 times greater than that obtained in irradiation of silica–alumina alone to the same dose.[6] From such results it was argued that the yield of trapped positive holes is limited by the availability of electron traps; O_2, CO_2, and N_2O, when present during irradiation, function as additional traps for mobile electrons and thereby enhance the visible coloration and positive-hole esr signal. Results obtained in the present work are consistent with such results and conclusions of the esr study and provide still more evidence for involvement of trapped positive holes in the dealkylation of isopropylbenzene. With increase in radiation dose to silica–alumina in the presence of O_2, it was found that the benzene yield (from subsequent exposure of the irradiated solid to isopropylbenzene) increases and attains a plateau at a dose about the same as that required for attainment of the plateau in irradiation of silica–alumina alone. The plateau yield obtained with O_2 present during irradiation,

cf. experiment 6, is 3 times greater than that in experiment 1. Such results, and the results of experiments 9 and 12, indicate that the benzene yield from silica–alumina irradiated alone, like the yield of trapped positive holes, is limited by the number of preexisting electron traps. The approximate equality of plateau yields in experiments 6, 9 and 12 suggests that (1) O_2, CO_2, and N_2O trap mobile electrons only at certain surface sites (that are limited in number) and remain bound to, thereby blocking, the site or (2) the number of preexisting positive-hole traps becomes the limiting factor with the electron scavengers present during irradiation. It is interesting that, as shown in experiments 8 and 10, the presence of electron scavengers during irradiation enhances the yield of only those dealkylation centers that are removed by exposure to H_2. Experiment 7 shows that electrons trapped by irradiation in the presence of O_2 are not freed by a second irradiation after pumping O_2 from the reaction cell.

On exposure of irradiated silica–alumina to CO or SO_2, height of the positive-hole esr signal decreases to ~85% of the original value and there is a slight bleaching of the visible coloration;[6] as shown in experiments 21 and 23, there is a corresponding small reduction in benzene yield. Because of the absence of visible coloration on irradiation of silica–alumina in the presence of CO or SO_2 and the appearance of a very intense new esr signal attributed to CO_2^- or SO_3^-, respectively, it was suggested that CO and SO_2 are very effective traps for the mobile positive hole (unstabilized O^-).[6] Thus, equality of the benzene yields in experiments 1, 20, and 22 suggests that the positive holes trapped by CO and SO_2 also are effective in isopropylbenzene dealkylation (the total yield of trapped positive holes and, therefore, of benzene being limited by the number of preexisting electron traps).

Results of the present study, then, provide strong support for the ideas developed in previous work.[2-6] The yield of benzene from contact of isopropylbenzene with irradiated silica–alumina, like the yield of trapped positive holes, does indeed appear to be limited by the number of preexisting electron traps. The total results seem to require that electron transfer from isopropylbenzene to a trapped positive hole (of any kind contributing to the esr spectrum) be the primary process in isopropylbenzene dealkylation on γ-irradiated silica–alumina.