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RADIOLYSIS AND PHOTOLYSIS IN THE ADSORBED STATE

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Abstract—Simultaneous irradiation of gases or liquids adsorbed on high-surface-area solids of insulator or semiconductor properties frequently produces a considerable increase in radiolysis yields and selective effects in the distribution of products in comparison with those obtained by irradiation of pure substances. This kind of reaction is also sometimes observed when the solid is irradiated before adding the reactant. The results show that part of the energy absorbed by the solid is transferred by some mechanism to the adsorbate and is able to cause its decomposition. In the present paper some of the most representative experiments in the field are analyzed, with special attention on the interpretation of results and proposed reaction mechanisms.

DURING the last decade some attention has been drawn to the action of ionizing radiation on heterogeneous systems consisting of a liquid or gaseous phase adsorbed on a solid of large area. Only limited information is available, and many points still remain obscure. Reviews of the more significant work have been given by Taylor [1], Coekelbergs *et al.*[2], and more recently by Polak and Pshezhetsky [3].

Our intention in this paper is to summarize the present information on the subject, including some papers recently published, and to relate our experience in the field, with special emphasis on the reaction mechanisms proposed.

Investigation in this field proceeds along two major lines. The first is concerned with the reactions produced by irradiation of the heterogeneous system, and the second with the chemical reactions occurring when solids have been irradiated before being brought in contact with the other phase. This second has received less attention, but its study is promising for the interpretation of mechanisms.

Different chemical reactions are known to proceed by irradiation of heterogeneous systems. Their most important characteristics are a considerable increase in reaction yields and a marked selectivity for final products, compared with radiolysis of the homogeneous phase. For low coverage of the solid surface, yields commonly increase from 5 to 10 times. If a chain reaction is induced, increases may be higher.

According to the terminology of Coekelbergs *et al.*[2], who discussed the calculation of G values in heterogeneous radiolysis, the G values calculated relative to the energy adsorbed by the whole system are called G_{het}, G_{ads} is the value calculated relative to the energy adsorbed by the adsorbate, and G_{hom} is the yield in homogeneous-phase radiolysis for a liquid or gas.

Table 1 gives examples of yields in different solids.

The increase in yield in heterogeneous systems has been interpreted on the basis of transfer to the adsorbate of the energy adsorbed by the solid, in an adequate fashion to produce chemical reactions. The energy-transfer process may involve interaction of the adsorbed molecule with nonequilibrium charge carriers produced in the solid by ionizing radiation and trapped in some structural defects.

One possible mechanism, which includes interaction between these charge carriers and an adsorbed molecule, is as follows:

Table 1. Radiolysis of methanol adsorbed on different solids[4] (after Zhabrova *et al.*)

Solids	G_{H_2}	$G_{(CH_2O)}$	$G_{(CH_2OH)_2}$
SiO_2	67	30	28
Al_2O_3	65	27	38
$SiO_2Al_2O_3$	45	30	22
KF	48	43	52
ZrO_2	15.5	12	22
ZnO	22	3	13
NiO	2	—	—
Pt	–	2	2
Homogeneous radiolysis of methanol	5, 1	1,6	3,9

A molecule is adsorbed at a positive hole, leading to the formation of a positive molecular ion:

$$[M]+(+) \rightarrow [M_a]^+$$

This reaction may be followed by neutralization with an electron; if the energy released in the process is sufficient, dissociation may occur:

$$[M_a]^+ + e^- \rightarrow R + R_1$$

Another possible mechanism is the capture by a molecule of a trapped electron:

$$[M] + e^- \rightarrow [M_a]^-$$

and recombination with a positive hole:

$$[M_a]^- + (+) \rightarrow R + R_1$$

The process that actually takes place depends on the electron affinities of the molecule and the trap, and the ionization potential of the molecule.

Mechanisms of this type have been invoked by several authors, since the first work by Sutherland and Allen[5].

COLOR CENTERS AND CHEMICAL REACTIONS

Some irradiated solids show intense color, and a relationship between color centers and trapped electrons with corresponding positive holes has been established. In the case of quartz the color centers have been shown to be due to positive holes trapped by an oxygen atom adjacent to a substitutional Al atom[6–8] Boreskov *et al.*[9] proposed a similar structure for color centers in silica gel.

Color induced in SiO_2 and Al_2O_3 is bleached by H_2 adsorption[9–14], and final disappearance of the color corresponds to saturation of the adsorptive capacity. This provides another means to study interaction in the heterogeneous system, and rather conclusive evidence of reaction of adsorbed molecules with color centers has been obtained. Quantitative studies of adsorption in silicas with different Al content, the use of diffuse reflectance spectroscopy, u.v. bleaching, and thermal annealing have shown that adsorption takes place in these color centers [10, 14].

Color centers in the visible region are also partially responsible for isopropylbenzene dealkylation on preirradiated silica-alumina. Reduction in benzene yield after H_2 adsorption corresponds approximately to the number of H_2 molecules adsorbed. Similar reduction in benzene yield was observed after thermal annealing of the molecules adsorbed. Similar reduction in benzene yield was observed after thermal color[15].

Nitrogen production proportional to SiO_2 decolorization has been observed after treatment with limited amounts of azoethane [16, 17].

Interaction with color centers showing adsorption in the u.v. region, corresponding to electrons trapped (E' and E''), has been tentatively proposed to explain dealkylation of isopropylbenzene of high purity SiO_2 irradiated at −196°C [18].

The mechanism involving interaction of adsorbed molecules with nonequilibrium charge carriers is also consistent with experiments using solids of different electronic properties and the same adsorbate and conditions. Insulators (SIO_2, Al_2O_3, KF, etc.) proved to be more efficient for energy transfer than semiconductors (MgO, ZnO, etc. [4, 17, 19]. Energy available for delivery to the adsorbate by recombination is not likely to be greater than the width of the forbidden band in the solid. A forbidden band gap greater than the dissociation energy of the molecule is necessary for decomposition. Insulators have a band gap of 8–10 eV and semiconductors of the order of 3 eV, whereas the dissociation energies of C—C and C—H bonds in alkanes are 3·4 and 4·4 respectively.

The energy transferred to the adsorbate for free-radical formation has been estimated in the SiO_2-hexane system to be about 5 per cent of the energy adsorbed by the solid if all the energy transferred is used for free-radical formation and 25 per cent if free-radical yield is the same as in the homogeneous phase [20].

PARAMAGNETIC SPECIES IN IRRADIATED SYSTEMS

Paramagnetic resonance is a useful tool for the study of radicals formed by irradiation in the solid and in the adsorbate. Interaction between both species can be studied by this technique.

Irradiation at low temperature of hexane adsorbed on silica gel shows that paramagnetic signals characteristic of the irradiated silica disappear with increasing surface coverage, while radicals from hexane increase correspondently [20]. Similar results have been obtained in the radiolysis of NH_3 adsorbed on Zeolites. The number of NH_2 radicals goes up with increasing concentration, while paramagnetic species from Zeolites decrease; when complete coverage is obtained, only NH_2 radicals are observed [21].

Radicals produced by irradiation and adsorbed on a solid surface show considerable thermal stability compared with those produced in a molecular matrix. They are not bound to the solid by the unpaired electron since they are detected by ESR, but differences in the spectra suggest that rotational motion is restricted due to adsorption. CH_2OH radicals on SiO_2 are stable for hours at room temperature [4]. Other examples are NH_2 in Zeolites [22] and C_2H_5 in SiO_2; recombination begins at temperatures 100°C higher than the melting points of NH_3 and C_2H_6 [22]. Methyl radicals produced by photolysis of CH_3I on Vycor glass are stable for several days at room temperature[23].

A low degree of surface coverage is essential for high stability of adsorbed radicals; when coverage reaches a monolayer or higher, recombination temperatures approach that observed in a molecular matrix [24].

SELECTIVITY IN HETEROGENEOUS RADIOLYSIS

A marked characteristic of heterogeneous-phase radiolysis is the selectivity for formation or suppression of some final products compared with that obtained in homogeneous radiolysis.

Caffrey and Allen[25] and Sutherland and Allen[5] observed an increase of branched products and suppression of unsaturates in the irradiation of pentane on SiO_2 or Zeolites. Unsaturates were also not observed in the radiolysis of heptane on Al_2O_3[11] and isopropylbenzene on silica-alumina[26]. In some cases strong adsorption of unsaturates in the solid made their recovery difficult. Reaction of adsorbed olefins by chain mechanism is an alternative explanation[27]. The disproportionation/recombination ratio of cyclohexane, which is 1:3 in the homogeneous phase, changes to 1:1 when cyclohexane is irradiated over silica gel[28]. More pronounced selectivity is always observed at low coverage of the solid surface; increasing coverage to monolayer or more suppresses the selectivity, and the distribution of products approaches that obtained in homogeneous radiolysis.

PRETREATMENT OF SOLIDS

Pretreatment of the solids has a definite influence in the results[28, 29]. Solids are generally degassed in vacuum of the order of 10^{-5}–10^{-6} Torr, at temperatures ranging from 20 to 900°C.

Considerable changes in the surface are produced by this treatment. In the case of silica gel the surface concentration of OH remains relatively constant up to 300°C, and decreases steadily at higher temperatures. Silica degassed at low temperature contains a large amount of silanol groups (SiOH); increase in temperature results in elimination of water, and silanol groups are replaced by siloxane (Si—O—Si). Decrease in area is also observed in gels heated at more than 750°C.

RESUMEN

La irradiación simultánea de gases o líquidos adsorbidos en sólidos de propiedades aisladoras o semiconductoras produce en la mayoría de los casos un considerable aumento de productos de radiólisis respecto a los producidos irradiando las substancias puras. Este tipo de reacciones también se produce a veces irradiando el sólido primero y agregando el reactante posteriormente.

Estos resultados muestran que parte de la energía recibida por el sólido es trasmitida por algún mecanismo a la fase absorbida y empleada en la desd composición del adsorbato.

En el presente trabajo se analizan algunas de las experiencias realizadas y se discuten los resultados e interpretaciones. Se discuten así mismo las posibilidades futuras en este campo.

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