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Radiation-Induced Catalytic Conversions

Organic Compounds Adsorbed on Solids of Different Electronic Properties

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The low-temperature radiation-induced conversions of methanol and cyclohexane adsorbed on solids were investigated. The solids used were dielectrics (SiO_2, silica-alumina, Al_2O_3, KF), semiconductors (ZnO, NiO), and metals (Pt, Pd). The samples were irradiated by γ-rays from Co^{60} at a dose rate of 4.5×10^{16} eV/g sec. Adsorption, kinetic, and ESR methods were used.

It was found that the highest activity was displayed by solids with a broad forbidden band, such as SiO_2, Al_2O_3, silica-alumina, and KF.

The maximum of radiation-induced catalytic conversion was observed at a low coverage of silica gel. Radiation-induced defects and surface-adsorbed radicals, namely $\cdot C_6H_7$ for cyclohexane and $\cdot CH_2OH$ for methanol were detected on insulators by means of the ESR technique.

For semiconductors the radiation yield was considerably lower. Metals had no effect on the reaction rates. Correlation between the radiation-induced activity of solids and the intensities of ESR signals due to adsorbed radicals was established. The amount of methanol decomposition products and of the radicals formed was studied as a function of the dose rate.

The possible mechanism of radiation-induced conversions in the adsorbed layer, involving electron and radical steps, is discussed.

Investigation of radiation-induced reactions occurring on solids of different electronic properties is of great interest both for elucidation of the energy-transfer mechanism, and for determination of the part played by conducting electrons, holes, and various labile forms, such as adsorbed radicals, in elementary steps of catalytic reactions.

The first group of problems is essential for radiation chemistry, the second for the theory of heterogeneous catalysis.

Extensive investigations on radiation-induced changes in electrophysical properties of solids have shown that the persistence of radiation-induced defects and of ionization effects was different for dielectrics, semiconductors, and metals (*1–3*).

In this connection attempts were made to analyze the effect of ionizing radiation on catalytic processes for catalysts of different electronic properties (*4, 5*).

However, up to the present there were, in fact, no experimental data on the use of insulators, semiconductors, and metals under the same conditions.

The given work is an attempt to find an approach to the solution of this problem. Solids with a different width of the forbidden band, such as insulators, semiconductors, and metals, were investigated, as well as a sample of activated charcoal.

Low-temperature radiation-induced decomposition of cyclohexane and methanol adsorbed on various solids was chosen for experiments. Decomposition of both substances appeared to be endothermic. It will be noted that homogeneous radiolysis of these compounds was studied extensively, and this made easier the comparison of radiation-induced yields.

TECHNIQUE

Use was made of the following solids: silica gel, alumina, silica-alumina, potassium fluoride, calcium oxide, zirconium dioxide, zinc oxide, nickel oxide, and disperse metals: platinum and palladium. An activated charcoal sample was also used.

Oxides were obtained by precipitation of hydroxides from nitrates by an alkali solution, with subsequent washing and annealing.

Specific surfaces were determined at room temperature by the BET technique, using cyclohexane or methanol as adsorbates. The specific surface of KF was determined from adsorption of krypton at $-196°C$.

The solids investigated were heated at 400°C in glass reactors supplied with break seals up to a vacuum of 10^{-5} mm Hg, and then were cooled to room temperature. Purified cyclohexane or methanol vapor was then admitted until a certain surface coverage was obtained. After that a small part of the sample ($\sim$100 mg) was poured over to a side ampoule soldered to the same system as used for ESR measurements. Then both the reactor and ampoule were sealed off and γ-irradiated from a Co^{60} source at temperatures of 293° or 77°K. The dose rate was 4.5×10^{16} eV/g/sec. The adsorbed energy dose varied from 8×10^{19} to 7×10^{21} eV/g. After irradiation the reactor was connected to the vacuum apparatus. The gas formed was admitted into the measuring part of the apparatus via a nitrogen-cooled trap. The main part of the gas appeared to be hydrogen, as shown by its diffusion through a heated palladium capillary.

Moreover, the gas contained small amounts of CH_4 and CO. As all condensed products were frozen off by liquid nitrogen, and special experiments have shown that under these conditions methane will not decompose on the hot palladium capillary, it may be considered that the method used for hydrogen determination gave correct results. In the case of cyclohexane decomposition the products formed and the unreacted compound were removed from the catalyst surface by heating to 100°C, and then were analyzed chromatographically. The formaldehyde formed in methanol decomposition was determined quantitatively in an aqueous extract by reaction with chromotropic acid using the McFaden technique (*6*). Ethylene glycol was oxidized to formaldehyde with periodic acid, and the iodates and periodates formed were reduced to iodides with excess tin dichloride for decoloration of the solution. Formaldehyde was determined as described above.

ESR studies were made in paralled with catalytic radiation experiments. Irradiation was conducted and spectra were obtained at 77°K.

The radiation yield G was calculated only with respect to the portion of energy taken up by adsorbed substances. An assumption was made according to Coeckelbergs and others (*4*) that cyclohexane and methanol were completely adsorbed at the catalyst surface during irradiation, and that energy was distributed among the adsorbed compounds and the solids in proportion to their electron fraction.

RESULTS

Comparison was made of radiation-induced yields in homogeneous and heterogeneous reactions. The yields of heterogeneous reactions occurring at dielectric surfaces were found to be considerably higher than those of homogeneous radiolysis of the organic compounds studied. This result, first obtained for radiation-induced cyclohexane conversion in the adsorbed layer (*7, 8*) and later confirmed for heterogeneous radiolysis of methanol (*9*), is in agreement with the results of other workers (*10–13*).

Experimental data on radiation-induced activities of various solids in methanol decomposition are listed in Table 1. It will be seen from the table that for many solids the radiation yield in the three main products (hydrogen, formaldehyde, and ethylene glycol), calculated allowing for the energy taken up by the adsorbed compound, are considerably higher than for homogeneous radiolysis. This is particularly evident for silica gel, silica-alumina, aluminum oxide,

TABLE 1

DATA ON RADIATION-INDUCED CATALYTIC CONVERSION OF METHANOL ON SOLIDS OF VARIOUS ELECTRONIC PROPERTIES ($T = 20°C$)

Solids	Forbidden band width ΔH (eV)	References	Specific surface S (m²/g)	Coverage θ (%)	Yields (molec/100 eV)[a]		
					$G(H_2)$	$G(CH_2O)$	$G(CH_2OH)_2$
SiO_2	8	*14*	270	50	67	30	28
Al_2O_3	7.3	*15*	300	50	65	27	38
$Al_2O_3 \cdot SiO_2$	—	—	170	50	45	30	22
KF	10.3	*16*	0.3	100	48	43	52
CaO	7.5	*17*	40	50	22	6	21
ZrO_2	4.8–5.1[b]	*18*	270	50	15.5	12	22
ZnO	3.3	*19*	50	50	22	3	13
NiO	2	*20*	50	50	2	—	—
Pt	—	—	40	60	—	2	2
Pd	—	—	29	50	—	1.5	2.5
Activated charcoal	—	—	800	50	0.1	0.5	0.4
Homogeneous radiolysis	—	—	—	—	5.1	1.6	3.9

[a] As a rule the yields are those obtained at low doses of absorbed energy. Only for small amounts of the products formed were the yields obtained at high doses.

[b] The ΔH value of 5.1 for ZrO_2 was obtained in our experiments from the threshold of adsorption in the UV (at $\lambda < 240$ mμ).

and potassium fluoride. For these compounds the results obtained seem to show that the ionizing energy taken up by a solid is transferred to the molecules adsorbed at its surface. On the other hand, the radiation yields for Pt, Pb, NiO, and activated charcoal do not differ appreciably from the homogeneous radiolysis yield, and this seems to show that there is no energy transfer in this case.

Certainly, this regularity is of a qualitative nature only, since a part of the methanol decomposition products (for example, hydrogen) may become strongly adsorbed by the surface and may distort the numerical values of G. However, the difference between solids of the first and second group is so great that it does not seem to be accounted for by different adsorption capacity only.

A possible explanation for the capacity of solids to transfer the absorbed energy to molecules at the surface will be given in the discussion of the results obtained. It will be noted only that the mechanism of this phenomenon seems to be related to electronic properties of solids, in particular to the width of their forbidden bands, though this dependence is of a rather complex nature.

In order to find out the regularities of energy transfer it was of interest to determine the conversion degree as a function of surface coverage. Figure 1 shows the degree of radiation-induced conversion of cyclohexane adsorbed on silica gel and the hydrogen yield as functions of the surface coverage (0.5 to 300% of the monolayer). It was established beforehand that no hydrogen was evolved during irradiation of pretreated silica gel (within sensitivity of the technique used).

It will be seen from Fig. 1 that low surface coverage corresponds to maximum radiation yield with respect to cyclohexane conversion. The yield in hydrogen decreases with increasing coverage, while the total amount of hydrogen evolved per 1 g of silica gel builds up slowly. The same is observed for heterogeneous radiolysis of methanol on SiO_2 (Fig. 2). In this case the dependence is even more marked.

At low coverage of silica gel the degree of methanol conversion to formaldehyde and ethylene glycol was about 21%; after completion of the monolayer it was 0.4% only. The conversion of pure methanol induced by homogeneous radiolysis was 0.1%

Moreover, at low coverage the radiolysis

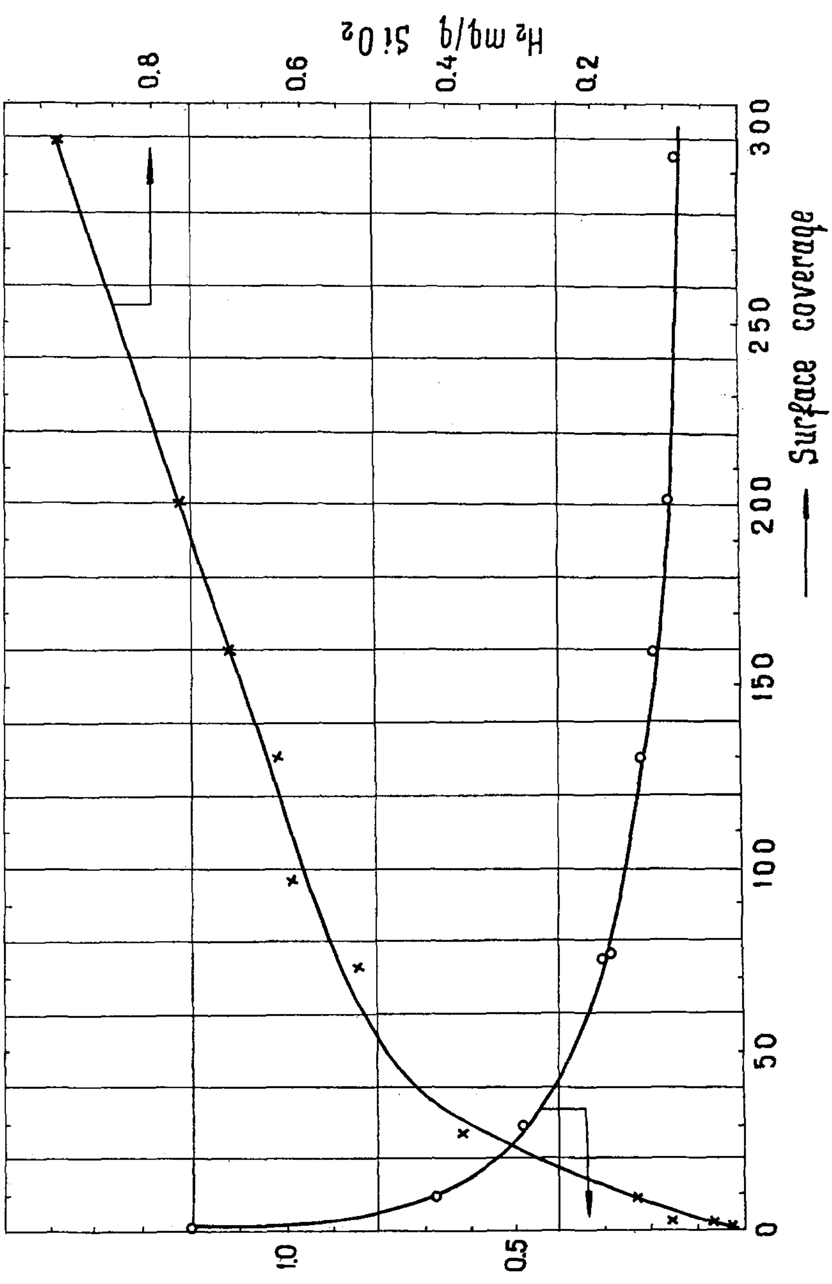

FIG. 1. Hydrogen yields (×) and degree of conversion with respect to hydrogen (○) as functions of the cyclohexane surface coverage; temperature, 20°C; dose, 5.4×10^{21} eV/g.

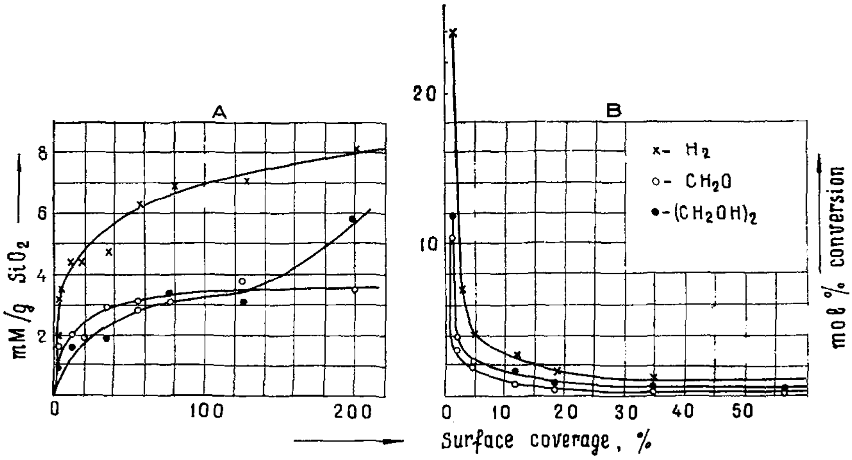

FIG. 2. The amount of hydrogen, formaldehyde, and ethylene glycol found (a) and the degree of methanol conversion with respect to these products (b) as function of silica gel coverage with methanol; temperature, 20°C; dose, 1.6 × 10^{20} eV/g. In calculating the radiation-induced hydrogen yields, allowance was made for radiochemisorption of hydrogen on silica gel, as established experimentally.

selectivity shifted towards predominant formation of formaldehyde with a simultaneous decrease in the ethylene glycol fraction formed (*21*). At low coverage the molar ratio of formaldehyde to ethylene glycol (α) was 2, at a monolayer $\alpha = 1$, and for homogeneous radiolysis it was $\alpha = 0.4$. Thus, the difference in selectivity of homogeneous and heterogeneous radiolysis is greatest at low surface coverage, which is indication of the specific action of the solid surface.

Irradiation of pretreated silica gel, silica-alumina, and aluminum oxide without absorbates, at 77°K, resulted in the appearance of ESR signals due to radiation-induced defects. No ESR signals were observed upon irradiation of platinum and palladium powers, of nickel oxide, and of active charcoal that were not efficient in energy transfer. Consequently, for the two reactions studied there is a close relation between the efficiency of dielectrics in the radiolysis of adsorbed molecules and the appearance of radiation-induced defects. At the same time metals and certain semiconductors appear to be inert in the radiation-induced catalysis, and do not show changes in their paramagnetic properties upon irradiation.

Surface-adsorbed radicals were detected for most active solids at low temperatures (77°K). Decomposition of cyclohexane ad-

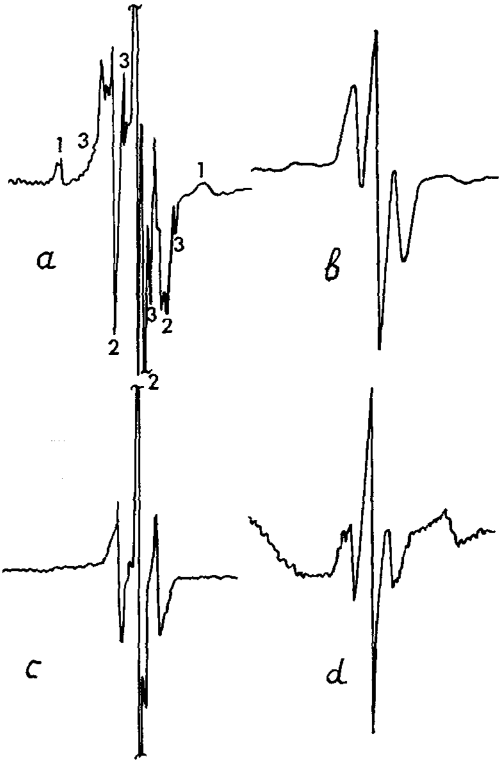

FIG. 3. ESR spectra of radicals formed by irradiation of methyl alcohol in an adsorbed state. Obtained at 77°K. (a) Spectrum of radicals adsorbed on SiO_2, 1, 2, 3, denote $\cdot CHO$, $\cdot CH_2OH$, and $\cdot CH_3$ lines, respectively; (b) spectrum of $\cdot CH_2OH$ adsorbed on Al_2O_3; (c) spectrum of $\cdot CH_2OH$ radicals adsorbed on SiO_2; (d) spectrum of $\cdot CH_2OH$ adsorbed on ZnO.

sorbed on silica gel, aluminum oxide, and silica-alumina yielded $\cdot C_6H_7$ (*7*, *8*), and that of adsorbed methanol resulted in the appearance of $\cdot CH_2OH$, $\cdot CHO$, and $\cdot CH_3$ radicals (*9*). ESR spectra exhibited by irradiated samples with methyl alcohol adsorbed on silica gel (Fig. 3a) showed a triplet with 20-gauss splitting, ascribed to $\cdot CH_2OH$ (*22*), an asymmetric doublet with a 69-gauss splitting (*23*) corresponding to $\cdot CHO$ radicals detected in a somewhat lesser amount, and very weak lines from adsorbed methyl radicals. ESR signals from adsorbed $\cdot CH_2OH$ radicals were also observed for irradiated aluminum oxide (Fig. 3b) and for zinc oxide with surface-adsorbed methanol (Fig. 3c). The high thermal stability of $\cdot CH_2OH$ radicals adsorbed on SiO_2 and on Al_2O_3 will be noted. At room temperatures these radicals did not disappear for dozens of hours. Irradiated samples of nickel oxide and active charcoal gave, in fact, no ESR signals.

These results show that there is qualitative correlation between the efficiency of insulating solids in heterogeneous radiolysis and the appearance of ESR signals corresponding to surface-adsorbed radicals.

A question naturally arose whether adsorbed radicals represented active intermediates of heterogeneous radiolysis.

This could have been verified by comparing absolute amounts of radicals with the yield in end products. Indeed, if all end products of radiolysis are obtained from radicals adsorbed at the primary step of radiolysis, at low irradiation doses, when the part played by secondary processes is unimportant, these values would coincide.

A series of runs was carried out under strictly identical conditions. This permitted correlation of the amounts of radicals and of the methanol decomposition products. Silica gel with a specific surface of 600 m^2/g was used as carrier in all experiments that were conducted at 77°K. The coverage of surface with adsorbed methanol was 30%.

It was found that in the range of low doses the curves for yields in adsorbed CH_2OH radicals and in ethylene glycol tend to approach each other (Fig. 4). The slopes of these curves at the origin differ by 1.5 to 2 times only; this may be considered as fair agreement, taking into account that not all

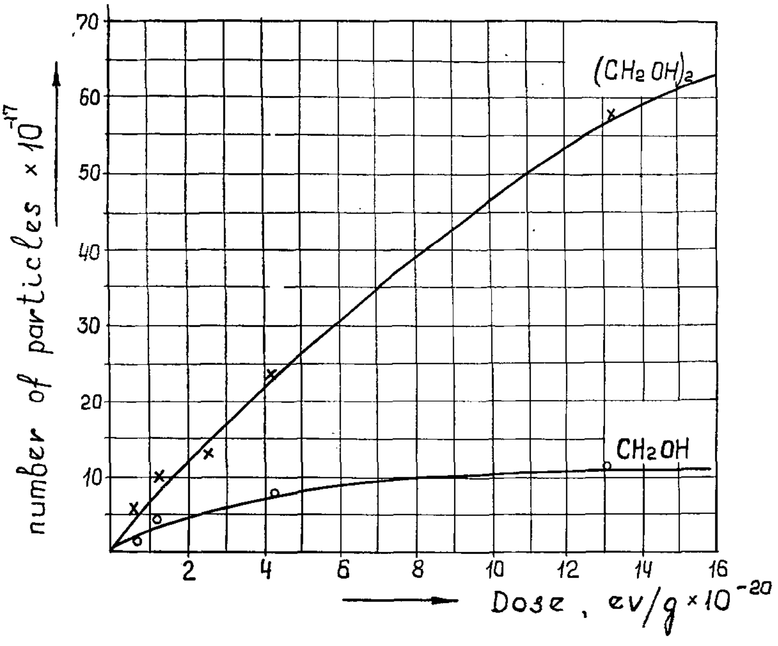

FIG. 4. The amount of $\cdot CH_2OH$ and ethylene glycol molecules as a function of the dose adsorbed at T = 77°K.

radicals formed are stabilized at the surface. With increasing doses of adsorbed energy the amount of $\cdot CH_2OH$ tended to a limiting value of 1×10^{18} g^{-1} while the increase in ethylene glycol with greater doses appeared to be continuous (Fig. 4). The limiting value for the amount of radicals as a function of the dose seems to be due to their recombination, with subsequent conversion to stable products. It will be of interest to note that with a lower surface coverage the amounts of $\cdot CH_2OH$ and ethylene glycol became closer, even for higher doses of adsorbed energy.

Discussion

Let us discuss now the possible mechanism of radiation-induced catalytic conversion of adsorbed organic compounds, in particular of methanol.

The main portion of the ionizing radiation energy is absorbed by the solid in the form of excited electronic states leading to formation of the carriers of excess charges.

Apparently, surface-adsorbed methanol molecules react with nonequilibrium current carriers created in solids by ionizing radiation. As adsorption of most organic compounds is of a donor nature, it may be suggested that the methanol molecule is adsorbed at the hole and is trapping it. The adsorbed charged molecule of methanol represents a center for recombination of the excess electron coming from the conduction band. Recombination of two charges releases energy in an amount determined by the forbidden band width, minus the heat of methanol adsorption. This energy becomes imparted to the adsorbed molecule and causes dissociation of the latter to $\cdot CH_2OH$ and $H\cdot$ radicals. The scheme of radiation-induced methanol decomposition at the surface of a catalyst may be represented as follows:

$$\text{Solid} \rightsquigarrow \text{Solid}, \oplus, \ominus$$

$$CH_3OH + \oplus \rightarrow CH_3OH^+$$

$$CH_3OH^+ + \ominus \rightarrow \dot{C}H_2OH + \dot{H}$$

Another possibility is the dissociation of adsorbed molecules due to their reaction with holes, and subsequent recombination of charged chemisorbed species.

$$\frac{CH_3OH}{\oplus} \rightarrow CH_2OH^+ + \dot{H}; \frac{CH_2OH^+}{\ominus} \rightarrow \dot{C}H_2OH$$

and so on

or

$$\frac{CH_3OH}{\oplus} \rightarrow \dot{C}H_2OH + H^+; \overset{H^+}{\underset{\ominus}{\rightarrow}} \dot{H}$$

$$\dot{H} + \dot{H} \rightarrow H_2$$

In accordance with both mechanisms, solids with a forbidden band greater than the C–H bond dissociation energy display a radiation-induced activity. Insulators and certain semiconductors are such solids.

The above suggestion following from the mechanism discussed seems to be in actual agreement with the experimental results obtained. Indeed, as mentioned above, the effect of energy transfer is particularly important for solids with a broad forbidden band, such as silica gel, aluminum oxide, silica-alumina, and potassium fluoride. Conversely, energy transfer is not observed for metals, nickel oxide, and activated charcoal. These solids either display a narrow forbidden band (NiO), or the given mechanism is in general invalid for them.

Certainly, the mechanism considered is very schematic and does not allow for many peculiarities of real solid structures, such as the impurities, different heats of adsorption of initial molecules, end products on adsorbent surfaces, etc. In this connection the difference between compounds with a forbidden band width close to the C–H energy (3 to 4 eV) might be not very marked (ZnO, ZrO_2). Precise evaluation of the catalytic activity boundary awaits further investigation.

It was shown above (*24*) that the radicals formed seem to be intermediates appearing in elementary steps of radiation-induced catalytic reactions. The recombination of $\cdot CH_2OH$ radicals would result in the formation of an ethylene glycol molecule.

$$\cdot CH_2OH + \cdot CH_2OH \rightarrow (CH_2OH)_2$$

Such reactions are predominant at high surface coverage, and also in homogeneous radiolysis. At low coverage the recombination of radicals is hindered and this seems to decrease the ethylene glycol yield and to favor the formation of formaldehyde. Taking into account the capacity of radicals for being current carrier acceptors (*25*), the capture of a hole by a $\cdot CH_2OH$ radical and subsequent recombination with one electron may be conceived. This might involve the formation of a formaldehyde molecule and a hydrogen atom.

It was of interest to find out whether the CHO radicals were intermediates in the formation of formaldehyde, or secondary products of formaldehyde radiolysis. Two parallel experiments were conducted in this connection. In the first experiment formaldehyde was formed on the silica gel surface by radiation-induced conversion of methanol. In the second experiment the amount of formaldehyde adsorbed on silica gel was taken equal to that in the first experiment. In both cases the amount of $\cdot CHO$ radicals formed was of the same order of magnitude, which was taken as evidence that $\cdot CHO$ radicals represented secondary product in the decomposition of formaldehyde formed by radiation-induced catalytic conversion of methanol.

Certain general conclusions may be made on the basis of the investigation discussed above.

Evidently, solids with a sufficiently great width of the forbidden band will be most efficient for radiation-induced reactions involving dissociation of a chemisorbed molecule to radicals, with subsequent conversions of the latter. This conclusion seems to be valid for many reactions in the decomposition of organic compounds. Other principles might govern reactions connected with the formation of ions on solid surfaces.

Maximum degree of conversion at low coverage, sometimes accompanied with changes in selectivity, is characteristic of many radiation-induced catalytic reactions occurring in the adsorbed layer at the surface of solids of the type of dielectrics.

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