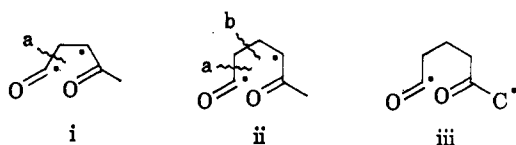


oxidation product of the ketol **12a**.⁹ The corresponding enol lactone **10b**⁸ afforded the diketone **11b**. Since the latter could not be isolated in pure form it was hydrogenated over platinum oxide to yield, *inter alia*, the ketol **12b**.⁹

The results of the irradiations of the enol lactones can be explained by assuming a primary cleavage of the carbonyl oxygen bond forming a diradical intermediate i, ii, or iii, respectively (mesomeric with the corresponding enol radicals). This cleavage is analogous to the one previously postulated in the conversion of enol esters.¹⁻³ The intermediate diradicals can be stabilized by: (i) direct recombination of the carbonyl radical with the "α-keto radical" to give a diketone; (ii) loss of carbon monoxide from the carbonyl part of the diradical and formation of a ring or double bond with the vinylic carbon atom (fragmentation a); (iii) cleavage of the C-C bond β to the carbonyl radical (fragmentation b).

The six-membered lactones with the exocyclic double bond give on photolysis products derived by process i only, and the five-membered endocyclic lactones products by process ii only. Since these enol lactones are readily obtained from the corresponding keto acids, the irradiation of both types of lactones can be used as a convenient synthetic route for the preparation of the corresponding bridged diketones and vinyl ketones. The irradiation of the six-membered endocyclic enol lactones afforded products derived by all three processes. Although no α-acetylcyclobutanone could be identified among the irradiation product of **3**, a coloration with ferric chloride solution was observed in the total reaction mixture which could indicate the formation of this derivative. On the other hand, the dimeric



material isolated from irradiation of **8** could be an artifact resulting from dimerization of the α-methylene ketone¹⁰ obtained by loss of ketene from **6**.

It seems that the cleavage of the enol lactones to a diradical intermediate is the preferred one when irradiated by a comparatively low wave length light. On the other hand, a related reversible photoconversion of non-enolic cyclohexane-1,3-diones to the exocyclic enol lactones has recently been reported using a longer wave length source.¹¹ It is pertinent to mention that the enol lactones show electronic transitions at λ_{max} 230-245 mμ,¹² not far from the main wave length

(9) The ketols **12a** and **12b** were obtained by lithium tri-*t*-butoxyaluminum hydride reductions of the corresponding enol lactones **10a** and **10b**, respectively; to be published later. Cf. J. Martin, W. Parker, and R. A. Raphael, *J. Chem. Soc.*, 289 (1964).

(10) Dimerization of analogous α-methylene ketones is well known; cf. E. Romann, A. J. Frey, P. A. Stadler, and A. Eschenmoser, *Helv. Chim. Acta*, **40**, 1900 (1957).

(11) H. Nozaki, Z. Yamaguti, and R. Noyori, *Tetrahedron Letters*, 37 (1965); R. C. Cookson, A. G. Edwards, J. Hudec, and M. Kingland, *Chem. Commun.*, 98 (1965).

(12) These transitions are seen in the o.r.d. and c.d. curves of the optically active enol lactones; to be published later. Cf. H. Wolf, *Tetrahedron Letters*, 1075 (1965).

emitted by the low pressure mercury lamp (254 mμ) used in the experiments described here.

(13) Taken in part from the Ph.D. thesis submitted to the Scientific Council of the Weizmann Institute of Science.

Amnon Yogev,¹³ Yehuda Mazur

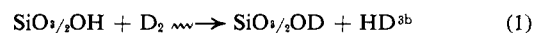
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γ-Radiation-Induced Exchange of Deuterium with Silica Surfaces¹

Sir:

A recent article describing the radiolysis of azoethane adsorbed on silica gel and magnesium oxide implied a certain model for γ-ray energy transfer phenomena.² Very briefly, radiation-produced excitations in the solid are assumed to migrate rather large distances, during which time volume defects compete with surface states for the excitation energy. It was interesting to see whether this model could apply to the direct isotopic exchange radiolysis of silica gel^{3a}



In particular, the variation of the HD yield as a function of crystal form, dose rate, purity, and particle size or surface area might reveal how far and how well the radiation energy could migrate.

The experimental techniques were similar to those described.^{3a} Three low-area silicas, α-cristobalite, vitreous silica, and quartz,⁴ were prepared by grinding appropriate materials. Silica gel of reduced surface area was prepared from Fisher silica gel by steaming or treating with ammonia. Surface areas were determined by N₂ adsorption and are given in Table I, column 2. Samples were degassed overnight at 410° before the first irradiation and annealed at 350° between irradiations. Samples were irradiated with ⁶⁰Co γ-rays or 2-Mev. Van de Graaff electrons to doses of 0.5 to 3 × 10²⁰ e.v./g. and at dose rates varying from 10¹⁸ to 3 × 10²¹ e.v./g. min. H₂, HD, and D₂ were determined gas chromatographically.⁵ Since there was considerable overlap of the H₂ and HD peaks, the gel was not deuterated as in ref. 3a; rather deuterium reacted with the protium gel. The 100-e.v. yields of exchangeable surface hydrogen at lowest dose rates based on energy absorbed in the total system are given in Table I, column 4. As the dose rate increased, the yield dropped monotonically to about two-thirds of the low dose rate value.

The 100-e.v. yields cited in Table I, column 4, assume that all the energy deposited in the solid is equally effective in causing reaction of the surface. A more reasonable assumption would be that only the energy

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) J. G. Rabe, R. Rabe, and A. O. Allen, *J. Am. Chem. Soc.*, **86**, 3887 (1964).

(3) (a) H. W. Kohn, *J. Phys. Chem.*, **66**, 1017 (1962). (b) This formula was used in ref. 3a. A more exact formulation would be SiO₂(OH)_x + yD₂ → SiO₂(OD)_y + yHD, where x and y depend on conditions of degassing. This reaction is of course followed by 2HD ⇌ H₂ + D₂.

(4) Mrs. Eleanor Pomerance of Oak Ridge and Vienna donated the oscillator-grade Brazilian quartz from her private collection.

(5) W. R. Moore and H. R. Ward, *J. Phys. Chem.*, **64**, 832 (1960).

Table I. $G_H (= G_{HD} + 2G_{H_2})$ for Reaction 1^a

Sample	Surface area, m. ² /g.	Frac-tion of mole-cules on surface	G_H , molecules/100 e.v.		
			Total energy ab-sorbed	Surface only	Ratio
α -Cristobalite	10.2	$1/128$	0.60	75	14.7
Vitreous silica	4.9	$1/260$	0.20	52	10.2
Quartz	4.0	$1/385$	0.06 ^b	20 ^b	3.9
Low area gel	80	$1/50$	0.60	30	5.9
Medium area gel	330	$1/4.2$	2.3	9.7	1.9
High area gel	550	$1/2.2$	2.3	5.1	1.0
Pure gel	425	$1/3.1$	2.3	7.1	1.4
SiCl ₄ prepn.					
Ultrapure gel	560	$1/2.2$	2.3	9.7	1.9
SiCl ₄ prepn.					
0.01 Al-SiCl ₄ prepn.	450	$1/3.0$	3.2	9.6	1.9

^a Samples degassed at 410° and annealed at 350° between irradiations; G values for lowest dose rates. ^b Maximum.

deposited in or near the surface results in chemical reaction. The fraction of the silica molecules on the silica surface can be calculated using only the density, surface area, molecular weight, and the formulas of elementary geometry. These fractions are gathered in the third column of Table I. Yields based on the energy absorbed only by these silica surface molecules can then be calculated by multiplying column 4 by the inverse of column 3, and are listed in column 5. Most of these "surface only" yields appear much too large; a more reasonable yield would lie in the range 3 to 6 molecules/100 e.v. Using 5.1 (the lowest "surface only" figure) as a reasonable estimate of the true yield, one can calculate a ratio by which the "surface only" yield is too great.

This ratio can be interpreted in several ways. If we assume that subsurface excitation events appear on the surface and result in the reaction of one or two molecules, the ratio gives the average number of subsurface layers participating in the reaction and hence the migration distance⁶ or the size of a collective excitation⁷ in molecular diameters. It does not seem reasonable that the size of a collective ionization should vary with particle size; indeed, one would expect that, as the particle size drops below that of a collective ionization, the yield would decrease, and this is not observed. Color centers do not afford a satisfactory explanation either since their yield is too low, and only those on the surface react⁸ (low-area silicas are blue after this reaction). On the other hand, if we assume that only excitations occurring directly on the surface are important, the ratio must be looked upon as the average length of a surface chain.⁹ Hence the most reasonable explanation for the ratio of column 6 of the table is that this number is the mean migration distance in molecular diameters or the average length of a surface chain. It is logically consistent that the energy mi-

(6) This terminology is based on the model in ref. 2. Similar treatment of the data for MgO in ref. 2 gives an average migration distance of 10 molecular diameters.

(7) This is the terminology of J. L. Magee, *Ann. Rev. Phys. Chem.*, **12**, 389 (1959).

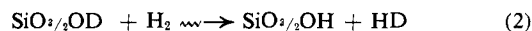
(8) H. W. Kohn, *J. Chem. Educ.*, in press.

(9) H. W. Kohn, *J. Phys. Chem.*, **68**, 3129 (1964).

gration distance does not exceed the particle size, or alternatively that the surface chain length does not exceed the number of surface molecules; *i.e.*, interparticle migration of intermediates is not required to explain the data.

The nature of the defects which compete with the surface for radiation energy is not explained by the data in the table. If regions of disorder or lattice defects dissipate energy, one would expect vitreous silica to be inferior as an energy-transfer agent to both α -cristobalite and quartz. It obviously is not. Impurities do not have an overriding effect on the yield either, especially on the "surface only" value.

We also note that the yields for reaction 1 are lower than those for the corresponding reaction



indicating that the yield-determining steps are initiated on the gel surface, and that diffusion is probably not yield determining.¹⁰ Both the isotope effect and the dose rate effect indicate that a reactant path and a deactivation process compete for reactive intermediates with reactions of different order.

Alumina and silica-alumina also show radiation-induced exchange decomposition like silica but the data at present are too fragmentary to include in this communication.

(10) N. H. Sagert (private communication) has observed a similar isotope effect in the system cyclohexane-silica gel; see also ref. 3a.

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Received June 1, 1965

Preparation and Properties of *i*-B₉H₁₅¹

Sir:

We wish to report that a new, unstable boron hydride is formed by treatment of KB₉H₁₄ with HCl at -80°. This hydride is thermally unstable and relatively indirect methods have been used to characterize it.

In a typical preparation, 0.150 g. of KB₉H₁₄ was treated with a measured excess of liquid hydrogen chloride at -78° for 30 min. in a sealed tube. No hydrogen was evolved during this time. Unreacted hydrogen chloride was distilled from the flask and final traces were removed by prolonged pumping at -50°. One mole of hydrogen chloride was retained by the reaction mixture per mole of salt used. The solid product was extracted with dry pentane and filtered using a chilled filtration apparatus. Decomposition with loss of hydrogen occurred at -30° or above, but analysis of the extract showed that no chloride was retained in the filtrate. A separately prepared sample was similarly extracted and treated with an excess of methanol for 9 hr. at 100°. The hydrogen formed in this reaction was measured volumetrically as a gas and the boron determined by titrating boric acid as the D-mannitol complex using the identical pH method. The observed ratio of hydrogen of alcoholysis to boron was 2.30, in good agreement with the theoretical 2.33 pre-

(1) Studies of Boranes. XIX. For paper XVIII of this series see D. MacLean, P. Keller, and R. Schaeffer, *Chem. Commun.*, in press.