

Since deuterium readily can be substituted for the bridging hydrogens, we have sought to test this hypothesis by repeated treatment of the samples with D₂O.

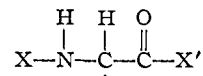
Powdered samples of glycylglycine and (glycyl)₂glycine have been treated with D₂O and then X-irradiated. Their resulting spin resonance patterns were found to be the same as those for the untreated samples. Comparative curves for glycylglycine are shown in Fig. 4. Similar comparisons were made of D₂O-treated and untreated samples of certain proteins—egg albumin, ovalbumin and pepsin—each of which upon irradiation at room temperature gives the characteristic doublet. Each was found to give the same doublet pattern after treatment with D₂O. The results are illustrated by the curves for egg albumin shown in Fig. 4. From these results we conclude that the characteristic doublet does not arise from the bridging NH hydrogen in the protein but from a hydrogen bonded to a CH hydrogen, which would not be replaced by the D₂O treatment.

It is interesting that rennin does not give the doublet resonance upon irradiation at room temperature but an incompletely resolved quartet. This pattern is not changed by treatment of the sample with D₂O (see Fig. 5). Thus the quartet structure must arise from protons bonded to carbon.

Measurements and analysis of the orientation-dependence of the doublet resonance in single crystals of untreated acetylglycine¹³ and of the orientation-dependence of the doublet resonance in silk strands and chicken feather quill¹⁴ indicate

(13) I. Miyagawa, Y. Kurita and W. Gordy, *J. Chem. Phys.*, **33**, 1599 (1960).

that this characteristic resonance arises from a free radical of the form



in which the electron spin is concentrated mainly on the α -carbon of the peptide chain. Here X and X' represent the remaining parts of the structure which do not measurably affect the resonance. The doublet splitting results, therefore, from the CH hydrogen, in agreement with the results reported here. Actually, our preliminary results on deuterium-substitution in glycylglycine and certain proteins were obtained before those of the orientation studies and were of assistance in the interpretation of the orientation effects.

A preliminary account¹⁵ of these studies was given earlier at a meeting of the American Physical Society. A similar study of deuterium substitution in the dicarboxylic series, HO₂C(CH₂)_nCO₂H, has been made by Box and Freund.¹⁶ We have also obtained results on these compounds, which will not be described since they indicate the same form of radicals as reported by Box and Freund, by Grant, Ward and Whiffen¹⁷ and by Heller and McConnell¹⁸ on single crystals.

(14) W. Gordy and H. Shields, *Proc. Natl. Acad. Sci. U.S.A.*, **46**, 1124 (1960).

(15) W. Gordy and I. Miyagawa, *Bull. Am. Phys. Soc. Series 2*, **4**, 227 (1960).

(16) H. C. Box and H. G. Freund, *ibid.*, **3**, 262 (1958).

(17) P. M. Grant, R. B. Ward and D. H. Whiffen, *J. Chem. Soc. (London)*, 4635 (1958).

(18) C. Heller and H. C. McConnell, *Bull. Am. Phys. Soc. Series 2*, **4**, 252 (1960).

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Radiolysis of Pentane in the Adsorbed State¹

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RECEIVED JULY 11, 1960

Pentane adsorbed on synthetic zeolites and on silica gel was exposed to γ -rays and yields of the various products were studied in detail as a function of pentane content. Radiolysis in the zeolite systems shows a number of peculiar features which depend on the nature of the positive ions present in the zeolite. Radiolysis of pentane adsorbed on silica gel is inhibited by the presence of small amounts of adsorbed salts. Skeletal isomerization is prominent in radiolysis of pentane on silica gel when the pentane content is low but is decreased by the presence of additional pentane or by lowering the temperature of irradiation. The results are discussed in terms of the behavior of excited electrons in solids.

Caffrey and Allen² found that the yields of products in the radiolysis of pentane by gamma rays were profoundly affected when the pentane was adsorbed on a chemically inert mineral solid of high surface area. Such effects are reminiscent of the effects of catalysts in directing reactions of organic compounds. Surface sensitization of radiolysis differs fundamentally from catalysis in that the reactions induced under radiation can as well move away from thermodynamic chemical equilibrium as toward it.

(1) Research performed under the auspices of the U. S. Atomic Energy Commission. A preliminary account of this work was presented at the Conference on the Uses of Large Radiation Sources in Industry, Warsaw, September, 1959, and will be published in the Proceedings of this Conference.

(2) J. M. Caffrey, Jr., and A. O. Allen, *J. Phys. Chem.*, **62**, 33 (1958).

The present work extends this study to a more detailed investigation of the silica gel-pentane system and to the radiolysis of pentane held in the lattice of synthetic zeolites or "molecular sieves." The zeolites have an open crystalline structure consisting essentially of a series of cages, the largest of which are connected together to form long tunnels through the material that can be penetrated by foreign molecules. Sodium ions, distributed through the cavities, can be replaced by other positive ions simply by immersing the substances in a salt solution. The zeolites therefore provide a large homogeneous adsorbing surface, the chemical nature of which is altered easily, and they seem particularly well suited to the systematic study of the effect of surface variables on radiolysis.

Experimental

The *n*-pentane was Phillips Research grade having a stated purity of 99.8%. No impurity peak was revealed by gas-liquid partition chromatography, which would appear to indicate that the purity was really higher than stated by the manufacturer. The silica gel was Fisher Scientific Co. 14-20 mesh, also used by Caffrey and Allen.² The synthetic zeolites were obtained from the Linde Co. One preparation was "Molecular Sieve 13X" powder composed of crystalline particles about 3 microns in diameter. This is the same substance described structurally by Barrer, Bultitude and Sutherland.³ The analysis of the dry material corresponds to $\text{Na}_2\text{O}\cdot\text{Al}_2\text{O}_3\cdot 2.67\text{SiO}_2$. The "tunnels" through the material have a maximum width of about 20 Å. and a minimum width of about 9 Å. The adsorptive capacity for *n*-pentane at room temperature is 0.45 cc. liquid pentane per cc. of crystal, or 4.4 molecules of pentane per cage, as calculated from the size of the structural unit cell.³ Ion-exchanged forms were prepared by stirring 30 g. of this material for two days at room temperature with 100 cc. of a solution of calcium, cobalt or manganous chloride containing approximately twice as much metal ion as would be equivalent to the sodium in the zeolite. The solid was filtered off and then washed with six portions of distilled water. The resulting products contained ions of the salt used together with some residual unreplaced sodium. Analysis of the calcium, cobalt and manganese zeolites showed that the atomic ratios of replacing ion to residual sodium were 0.94, 0.60 and 0.63, respectively. The respective percentages of sodium replaced by the divalent ions were 65, 55 and 56. The original and the three ion exchange preparations are here called NaX, NaCaX, NaCoX and NaMnX. Attempts to prepare iron and copper zeolites failed to yield heat-stable products.

Another sample of NaX was stirred with 1 M NH_4Cl for 3 hr., which resulted in replacement of 19% of the Na^+ ions by NH_4^+ . The sample then was heated to 400° in vacuum, which drove off all the ammonia, leaving 19% of the Na^+ ions replaced by hydrogen ions, H^+ . This material is here called NaHX. Direct replacement of Na^+ by H^+ is not possible since the structure of the material collapses when it is immersed in an acid solution.

Another synthetic zeolite used was Linde "Molecular Sieve 5A" powder, herein called CaA. The approximate formula of this material is believed to be $\text{Na}_2\text{O}\cdot 3\text{CaO}\cdot 4\text{Al}_2\text{O}_3\cdot 8\text{SiO}_2$. The largest channels in the structure have a minimum diameter of only 5 Å. In all these structures it is quite possible that although pentane molecules readily penetrate the structure, some of the radiolysis products of pentane may be unable to get out. We have attempted to determine only those radiolysis products which are distilled out of the material on heating in vacuum at 400°.

Some silica gel samples were stirred with 100 cc. of 1 M CoCl_2 or FeCl_3 solutions and were filtered, washed and dried. The resulting material contained 0.05% Co or 0.46% Fe. On heating in vacuum the iron sample turned brown, suggesting that at least part of the FeCl_3 was converted to Fe_2O_3 .

Prior to each run the water content of the solids was determined by heating to approximately 700° in air. All results are calculated using the weight of outgassed material. Four to five grams of solid was placed in a Pyrex tube 1.0 cm. i.d. and about 13 cm. long, fitted with a breakseal. The material was sealed onto a vacuum line and outgassed at 420-450° for four or five days, until the residual pressure was less than 2×10^{-5} mm. The material then was essentially free of water. A known quantity of pentane was distilled into the solid from a calibrated volume, and the tube was sealed off under liquid nitrogen. Greaseless valves were used throughout the vacuum system.

Irradiations were done with Co^{60} gamma rays at the Brookhaven Gamma-Irradiation Facility. Most of the irradiations were done at 25°, but one series using silica gel was performed with the samples packed in Dry Ice at approximately -78°. The dose rates were 0.25 to 0.35 megarads (Mr.) per hour. Total doses were 17 Mr. for the silica gel runs, 21.6 Mr. for the zeolite runs.

After irradiation the tubes were opened through break-seals and the gaseous products pumped through a liquid nitrogen trap into a McLeod gauge. The temperature of

the sample, which was initially that of the room, was gradually increased to 400° where it was maintained for 2 hr. to ensure as thorough removal of radiolysis products as possible. The non-condensable gas, which contained only hydrogen and methane, was analyzed by combustion over copper oxide. The fraction of pentane decomposed in the runs amounted to at most 3.5% and was much less in the majority of the runs, so that the liquid product recovered was mainly undecomposed *n*-pentane. Aliquots of the liquid product were taken in micropipets, the temperature during sampling being kept at -78° to avoid loss of volatile compounds. Analysis was performed by gas-liquid partition chromatography on a Perkin-Elmer "Vapor Fractometer" Model 154, using a 4-meter "UCON" column (polypropylene glycol) calibrated by passing known quantities of the various hydrocarbons under the conditions of temperature and flow rate used in the radiation product analyses. The determinations were believed to be accurate to about 10% for the products occurring in the largest yields, 20% for products having a yield G_T around 0.05 and poorer for products of still lower yields. For comparison with the runs on adsorbed pentane, samples of liquid pentane sealed in ampoules under vacuum were irradiated and analyzed in the same manner.

It was important to determine that the observed decomposition of pentane was really due to radiolysis and not to catalytic decomposition occurring during the outgassing. Conceivably the solid might be activated by radiation to a form more catalytically active than the normal. Therefore a large number of control experiments were run in which pentane was adsorbed onto the solids which had been preirradiated in vacuum, and the gas evolution was determined when the resulting mixture was heated to 400° to release the pentane. Results of some of these runs are given in Table I. In no case was any gas evolution noticed comparable to that produced by the radiolysis occurring when the pentane and solid were irradiated together.

TABLE I
RESULTS OF BLANK DETERMINATIONS

Solid	Irradiation in vacuo ^c	Treatment after outgassing Weight % pentane put into solid ^d	H_2 found, ^a $\mu\text{moles gas}^b$
SiO_2 gel	Yes	None	0.06
	No	1.8	0.5
	No	6.8	0.1
	Yes	2.2	1.6
	Yes	8.9	1.3
NaX	Yes	None	0.07
	No	2.3	0.7
	No	13.1	1.2
	Yes	6.0	1.3
NaCoX	Yes	11.9	1.6
	Yes	None	0.08
	Yes	6.5	0.4
	Yes	10.7	0.4

^a Where yields of gas were too low to determine hydrogen the total gas yields are given. ^b In typical irradiation runs hydrogen yields from the *n*-pentane-solid system ranged silica gel, 60-217 μmoles ; NaX, 14-28 μmoles ; NaCoX, 60-155 μmoles . ^c With 21.6 megarads of γ -rays. ^d When the solid was irradiated, the pentane was adsorbed after irradiation. The pentane was in all cases desorbed by heating the solid to 400°.

Results

Results of radiolysis of liquid pentane are shown in Table II, with yields published by Wagner⁴ and by de Vries and Allen⁵ given for comparison. The yield of hydrogen decreases somewhat with increasing dose. The yields of decane found in these experiments lie between those reported by Wagner for X-rays and for electron beams and are considerably lower than those reported by de Vries and Allen.

(3) R. M. Barrer, F. W. Bultitude and J. W. Sutherland, *Trans. Faraday Soc.*, **53**, 1111 (1957).

(4) C. D. Wagner, *J. Phys. Chem.*, **64**, 231 (1960).

(5) A. E. de Vries and A. O. Allen, *ibid.*, **63**, 879 (1959).

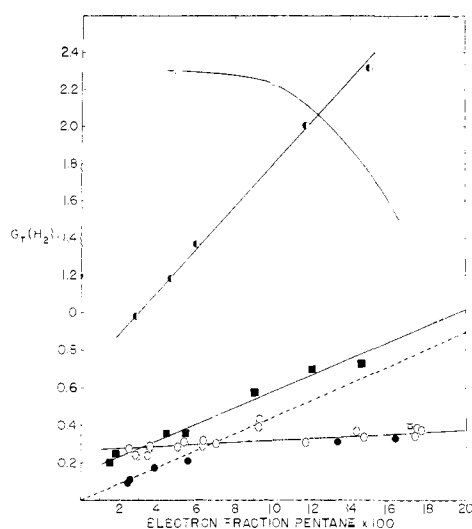


Fig. 1.—Hydrogen yields from pentane contained in zeolites: O, NaX; ●, NaMnX; □, NaCaX; ○, NaCoX; △, NaHX; ■, CaA, liquid line broken.

Data for the irradiation in the adsorbed state are expressed in terms of G_T , the number of molecules of product formed for each 100 e.v. of energy absorbed by the total system of solid plus pentane. These values are presented for each product as a function of the electron fraction of pentane in the mixture. Electron fraction is used rather than weight or mole fraction because it is believed that

TABLE II
YIELDS (G) OF PRODUCTS FROM RADIOLYSIS OF LIQUID PENTANE AT OR NEAR 25°

Radiation	Present work γ-rays			Wagner ⁴ 3 Mev. X-rays		DeVries ⁵ 2 Mev. e ⁻
	36	48	60	38	105	25-100
H ₂	4.17	3.71	3.5	4.1	4.20
CH ₄	0.22	0.22	0.24	0.22
C ₂ H ₄ + C ₂ H ₆65	.5963
C ₃ H ₈	0.59	.58	.6133
C ₄ H ₁₀	.09	.09	.1029
n-Butane	.12	.13	.1309
Butene-1 + isobutene	.02	.02	.0306
Butene-2 (trans)	.036	.029	.010
Butene-2 (cis)	.009	.013	.005
Pentenenes	...	1.02	1.1471
Isopentane	.08	0.08	0.07	0.05	0.04	Trace
n-Hexane	.02	.03	.06	.14	.052	0.14
Isohexanes	.11	.04	.34		.081	.03
n-Heptane	.07	.05	.05	.47	.09	.45
Isoheptanes	.25	.18	.21		.23	.41
n-Octane	.04	.03	.04	.43	.07	.20
Isooctanes	.19	.16	.19		.22	.59
n-Nonane	.003	.006	.006	.05	.014	.00
Isononanes	.07	.05	.03		.039	.21
n-Decane	.02	.05	.03	1.45	.06	.28
Isodecanes	1.29	1.11	1.01		.74	2.40

the initial deposition of the energy by the radiation in each component of a mixture is approximately proportional to the electron fraction of the component. If there were no interaction between pentane and solid and the specific radiolysis yield were the same in the adsorbed state as in liquid pentane, then a plot of G_T for each product against the electron fraction of pentane would be a straight

line running from the origin to the liquid G value at 100% pentane. This line is shown in the figures and is called the "liquid line." A point lying above the liquid line means that the amount of a product formed by exposure of adsorbed pentane to a given dose of gamma rays is greater than would be obtained from exposure of the same quantity of liquid pentane to the same dose of gamma rays.

Figure 1 shows the hydrogen yields obtained from pentane adsorbed on the different zeolites. The results from NaX, NaCaX and NaMnX appear to lie about straight lines, having a low slope and apparent positive intercept on the G_T axis. Slopes and intercepts are shown in Table III. The intercept is of course not physically realizable, since it was shown (Table I) that if no pentane were added to the solid essentially no hydrogen or other gas was obtained on irradiation. What the data show is that when a small amount of pentane is present a certain amount of radiolysis of the pentane occurs which is not greatly increased by adding more pentane. Yields of H₂ from NaHX were very much higher but appeared actually to decrease when the amount of pentane present was increased. The yields from CaA increased with increasing pentane content at the same rate as expected from the increasing direct absorption of energy by the pentane; that is, the slope of the CaA line on the graph is the same as that of the liquid line. In all these cases 80-95% of the hydrogen was obtained when the sample was first outgassed at room temperature, with the remaining small amount coming out on heating.

With NaCoX the results were quite different. Practically no gas was evolved at room temperature but on heating to 400° large quantities of hydrogen appeared, the amounts obtained being shown in Fig. 1 and Table III. This gas contained

TABLE III
LEAST-SQUARE LINES FOR $G_T(\text{H}_2)$ OF PENTANE ADSORBED ON ZEOLITES AS A FUNCTION OF ELECTRON FRACTION OF PENTANE IN THE MIXTURE (SEE FIG. 1)

Zeolite	Intercept (mol./100 e.v.)	Slope (mol./100 e.v.)
NaX	0.26	0.71
NaCaX	.28	0.58
CaA	.15	4.2
NaCoX	.68	11.1

1% of carbon monoxide which was not present in runs made with other solids. In one run, after the solid had been outgassed, the gas measured and the liquid products caught in a trap, the liquid was distilled back onto the cooled solid, which then was reheated to 400°. A new yield of hydrogen gas was obtained which amounted to about 20% of the previous gas yield but which now contained 26% of CO and no methane. The whole process then was repeated four more times; gradually decreasing amounts of hydrogen were evolved each time, and the CO content of the gas remained at 20-30%. The results suggest that with the other solids the products result directly from radiolysis, but in the presence of cobalt ions a more complicated reaction occurs, with the products finally observed resulting from reactions occurring after the irradiation during

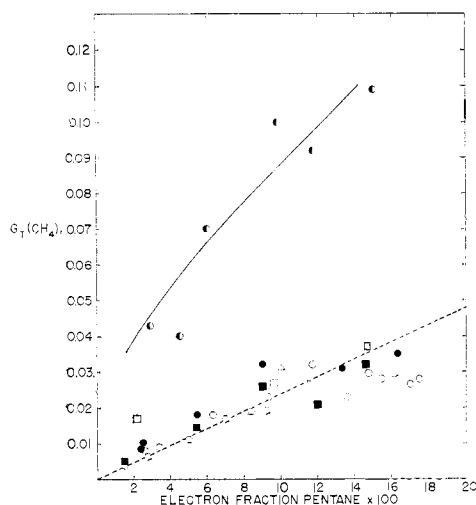


Fig. 2.—Methane yields from pentane contained in zeolites; meaning of symbols same as in Fig. 1.

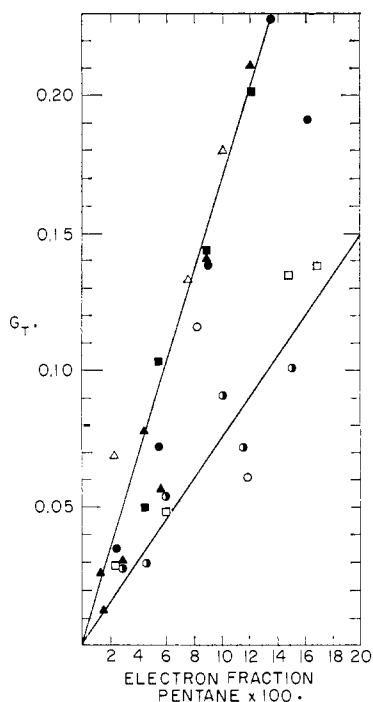


Fig. 3.—Ethane yields: O, NaX; ●, NaMnX; □, NaCaX; ○, NaCoX; ■, CaA; ▲, silica gel, 25°; △, silica gel, -78°.

the outgassing procedure. As shown above, these reactions did not occur when the solid was first irradiated under vacuum and pentane then added.

Methane yields from the zeolite preparations are shown in Fig. 2. Most of the results are close to the liquid line, indicating little interaction of pentane and solid with respect to those modes of reaction which lead to formation of methane. NaCoX and NaHX show higher yields, but all the yields are small compared to the yields of hydrogen.

Figures 3, 4 and 5 show the yields of ethane, propane and *n*-butane obtained from the zeolites (except NaHX) and include points also for silica gel. The various solids show much less difference from

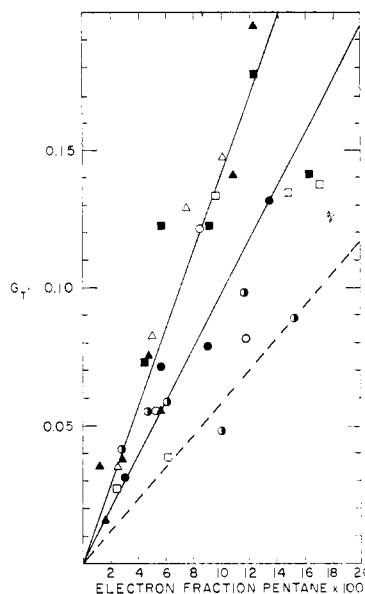


Fig. 4.—Propane yields; meaning of symbols same as in Fig. 3; liquid line broken.

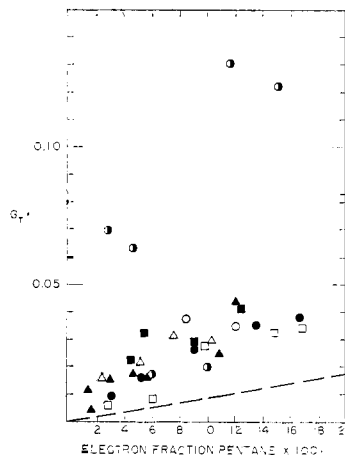


Fig. 5.—Normal butane yields; meaning of symbols same as in Figs. 3 and 4.

one another in these yields than is shown by the hydrogen yields. In all these cases the yields of the corresponding unsaturated hydrocarbons were much lower than those of the saturated.

On all the zeolites except NaHX the yields of products heavier than pentane were negligibly small. This may be attributed to inability of large molecules to emerge from the zeolite structure. With NaHX, however, relatively large yields of the heavier compounds were obtained and the detailed results of products of the radiolysis of this system are shown in Table IV. A reasonably good material balance was found in this analysis, showing that nearly all the products emerge from the zeolite structure. The difference in this respect between NaX and NaHX may be ascribed to the small size of the proton compared to the sodium ion, but it is surprising that replacement of only 19% of the Na ions by H could result in such a large difference in recoverability of decane. It is seen that hydrogen and decanes are the main products. Yields of un-

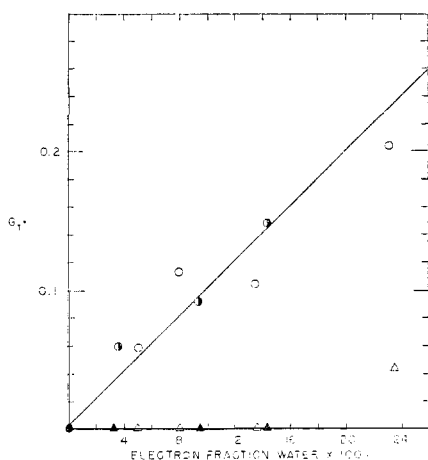


Fig. 6.—Radiolysis of water contained in zeolites; O, H₂ from NaX; ●, H₂ from NaCoX; △, O₂ from NaX; ▲, O₂ from NaCoX.

saturates and hydrocarbons of intermediate molecular weight are relatively low.

The intercepts of the hydrogen yield lines could be attributed to a trace of residual water remaining in the zeolite after outgassing at 400° if the energy absorbed in the mineral by the radiation were transmitted specifically to the water with very high efficiency. To see whether such a high yield existed, we irradiated samples of NaX and NaCoX to which various amounts of water were added. As seen in Fig. 6 the yield of hydrogen from the adsorbed water is low and increases in a regular way with water content, indicating that there is no preferential transfer of energy from the solid to adsorbed water.

TABLE IV

PRODUCT YIELDS FROM PENTANE RADIOLYSIS ON NaHX	Electron % pentane →		
	4.98%	10.0%	16.2%
	G _T values		
Hydrogen	2.31	2.24	1.57
Methane	0.13	0.03	0.03
Propane ^a	.11	.10	.17
Propene	.093	.032	.019
<i>n</i> -Butane	.037	.024	.078
<i>i</i> -Butane	.033	.001	.006
Butenes ^b	.52	.17	.05
<i>i</i> -Pentane	.08	.04	..
Pentenes ^c	.083	.015	..
Unknown ^d	.16	.02	..
Hexanes	.032	.01	.03
Heptanes	.074	.045	.049
Octanes	.035	.043	.019
Nonanes	.010	.008	.005
Decanes	1.48	2.04	.88

^a Ethane-ethylene yields doubtful because of intrusion of air peak. ^b Includes *cis*- and *trans*-butene-2, butene-1 and isobutene. ^c Chiefly *trans*-pentene-2, with some *cis*-pentene-2 and pentene-1. ^d May be a diene; see text.

Hydrogen yields from radiolysis of pentane adsorbed on silica gel are shown in Fig. 7, with data of Caffrey and Allen² given for comparison. The temperature of irradiation is seen to have little or no effect on the hydrogen yield. The presence of iron or cobalt salt on the surface markedly reduces the hydrogen yield, especially at high pentane con-

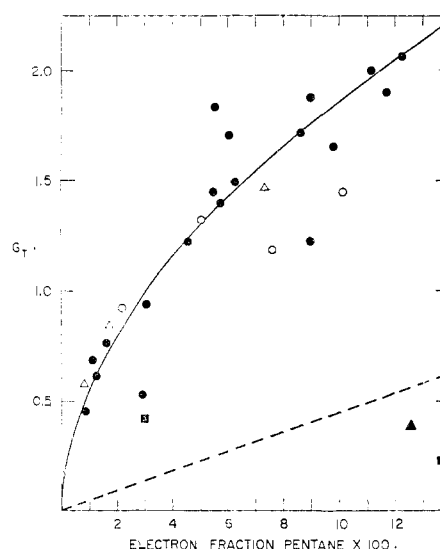


Fig. 7.—Hydrogen yields from pentane adsorbed on silica gel: ●, 25°; ○, -78°; △, data of Caffrey and Allen (25°); ▲, treated with FeCl₃; ■, treated with CoCl₂; liquid line broken.

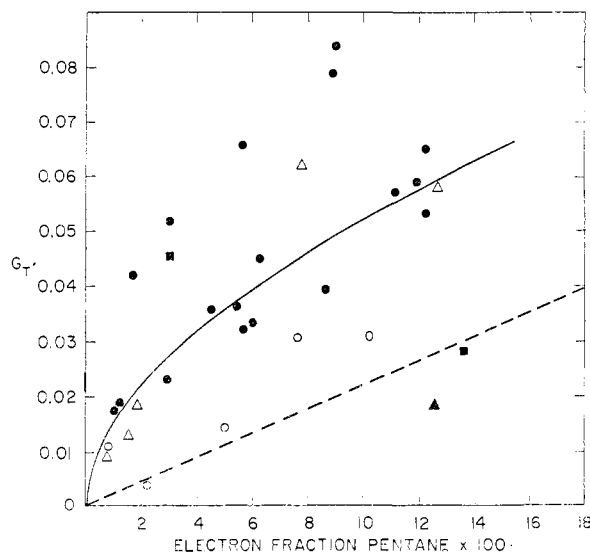


Fig. 8.—Methane yields from pentane adsorbed on silica gel; meaning of symbols same as in Fig. 7.

tent. Methane yields from silica gel-pentane are shown in Fig. 8. Yields are low and scatter badly, but it appears that the yield is reduced when the irradiation is carried out at a low temperature. The yields of ethane, propane and *n*-butane, shown in Figs. 3-5, are small and do not differ significantly from the results obtained with the zeolites.

The silica gel-pentane system does, however, give important yields of isobutane and isopentane, as shown in Figs. 9 and 10, which are not given by the zeolite systems. The yields of these products fall sharply as the amount of pentane present is increased, in contrast to the behavior of the other yields.

Figure 11 shows the yields of pentene from silica gel, this being taken as the sum of the yields of pentene-1 and *cis*- and *trans*-pentene-2, which ap-

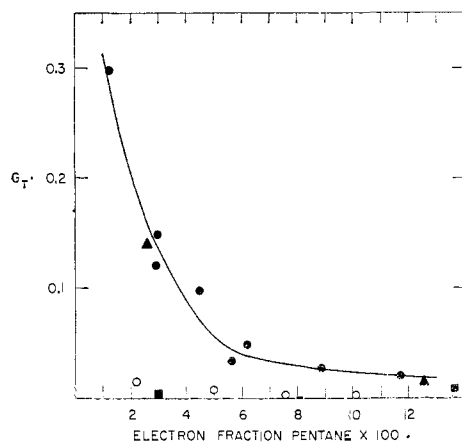


Fig. 9.—Isobutane yields from pentane adsorbed on silica gel; meaning of symbols same as in Fig. 7.

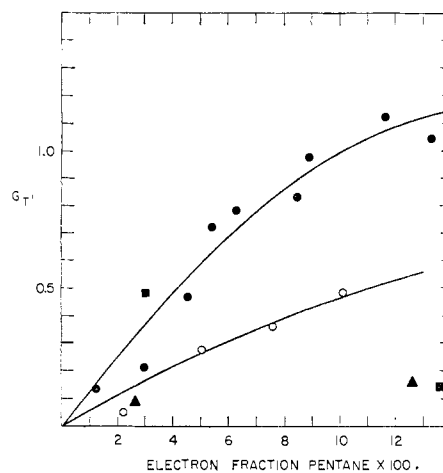


Fig. 12.—Yields of total decanes from pentane adsorbed on silica gel; meaning of symbols same as in Fig. 7.

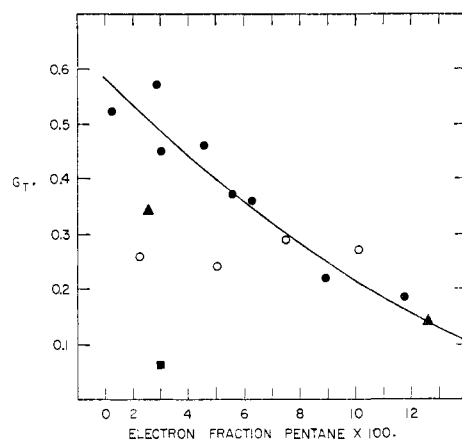


Fig. 10.—Isopentane yields from pentane adsorbed on silica gel; meaning of symbols same as in Fig. 7.

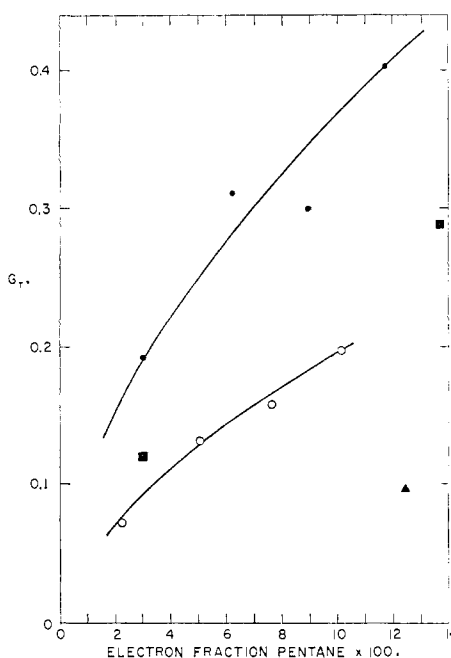


Fig. 13.—Yields of total hydrocarbons in the C_4 - C_6 range from pentane adsorbed on silica gel; meaning of symbols same as in Fig. 7.

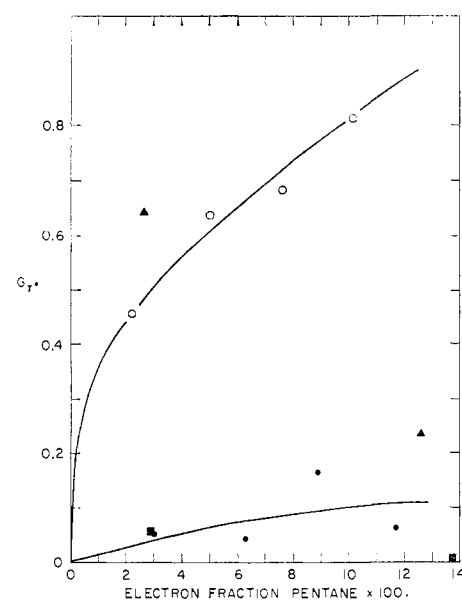


Fig. 11.—Yields of total pentene (pentene-1 plus *cis*- and *trans*-pentene-2) from pentane adsorbed on silica gel; meaning of symbols same as in Fig. 7.

peared as separate peaks on the chromatograms. The yield of pentene shows a marked increase when the irradiation is performed at low temperatures, while the yield of decane, shown in Fig. 12, decreases correspondingly.

Chromatograms of products from all the silica gel and NaHX samples showed a peak lying between the pentene peaks and the hexane peaks. This peak did not correspond to that of cyclopentane and it disappeared, along with other peaks due to the various unsaturated products, when a sample was treated with bromine before analysis. The substance responsible for this peak was not identified; it may be a diene. The G_T value for this substance appeared to be of the order of 0.1 for irradiations on silica gel carried out at 25° , 0.2–0.3 for irradiations at -78° .

Peaks corresponding to hydrocarbons in the C_4 to C_9 range also were found in the silica gel runs. The total number of such peaks was greater than with liquid pentane, a not unexpected result in view of the higher yields of isobutane and isopentane obtained on the gel. The yields of the separate compounds were all small and hardly worth presenting in detail. Figure 13 shows the sum of G_T values obtained for all the products in the range C_4 to C_9 for pentane irradiated on silica gel.

Discussion

As pointed out by Caffrey and Allen,² the yields obtained at low pentane content are so high that it would be very difficult to attribute them to energy taken up directly by the pentane from the radiation. Some method of transferring energy from the solid to the organic molecules must exist. Conversely, the increase in hydrogen yield when additional pentane is added to NaX and some of the other zeolites is so small that one suspects that the energy taken up by this additional pentane on irradiation is in some way dissipated in the solid. The processes occurring in these complicated systems are far from being well understood, but a hypothesis to explain some of the results can be formulated in terms of the states known to be available to excited electrons in solids.

The excitation of electrically non-conducting crystalline solids by radiation results in the release into the conduction band of electrons, of potential energy up to several e.v. and formation of the corresponding positive charges, or "holes" as they are called. Electrons and positive holes move about until they either recombine with one another or are trapped by impurities, lattice defects or surfaces. Perfect crystals possess definite "surface energy levels," having energies lying between those of the ground level and the conduction band, in which the electron wave function extends over the entire face of the crystal.⁶ An electron, freed by radiation and trapped in a surface level, will eventually combine with a migrating hole as irradiation continues, and the energy of the surface level would then normally be dissipated as heat. If an adsorbed molecule is present, however, it may interact with and distort the wave function of an electron trapped in a surface level. When such an electron is neutralized, the energy of neutralization may then appear as excitation of the adsorbed molecule, if an available level of this molecule exists at a lower energy than the surface level of the crystal. The excited molecule may then decompose.

This process may be responsible for the apparent intercept of the lines representing yield of H_2 as a function of pentane content in radiolysis on the crystalline zeolites. With increasing pentane content, the energy transferred to pentane through surface levels should remain about the same, but an increase in the yield results from energy absorbed by the pentane itself. The latter contribution is more effective in CaA than in NaX. It is tempting to suppose that a lower-lying surface level exists in NaX, which can take the excitation energy away from the more highly excited pentane molecules

and thereby partially protect the pentane against radiolysis.

In NaHX the hydrogen yields are much higher, and it is possible that hydrogen ions on the surface can trap electrons from the conduction band to form hydrogen atoms, which may then abstract hydrogen from pentane to yield H_2 and pentyl radicals. This process would leave an excess of positive charges in the solid, which could migrate to the organic part of the system, and thereby perhaps add to the radiolytic yield.

The yields from NaCoX seem to result from post-irradiation reactions and the mechanism is not understood. These peculiar effects did not occur in the silica gel which contained cobalt chloride, perhaps because the cobalt content was much lower in the gel preparation.

The conduction-band concept also applies to the irradiation of amorphous substances like glass⁷ and, presumably, silica gel. Because of the imperfect lattice periodicity, the range of the conduction-band electrons must be restricted to a few molecular diameters, and the surface levels must be highly localized. A surface-trapped electron will then affect adsorbed pentane only if it finds a pentane molecule in its immediate neighborhood. The yields of pentane radiolysis accordingly increase smoothly from zero as the pentane content increases. When salt is present in low concentration on the surface, the surface states are concentrated in the vicinity of these polar centers, so that the bulk of the pentane, adsorbed on the rest of the surface, is protected; and the yield of radiolysis is greatly decreased. The main reactions of the excited pentane are, apparently, either (a) to lose a hydrogen atom and form a pentyl radical, which eventually disappears chiefly by dimerization to decane; or (b) at lower temperatures to release a molecule of hydrogen leaving pentene behind. The temperature effect suggests that the release of the H atom requires a higher activation energy than the release of the H_2 molecule, which is not unexpected in view of the greater endothermicity of the former reaction. Entropy considerations favor release of the atom, so that this reaction predominates at the higher temperatures. However, according to Wagner's data⁴ the decrease in pentene yield with increasing temperature is not found in the radiolysis of liquid pentane.

The most striking effect in pentane radiolysis on silica gel is the isomerization of the carbon skeleton, which tends to be inhibited at higher pentane concentrations and at low temperatures. This may be explained in either of two ways, depending on whether the excited or ionized pentane molecules are thought to migrate freely over the surface of the silica or to remain fixed in position during their lifetime. In the former case it could be supposed that a pentane ion (either a carbonium or a radical ion) has to migrate to a special kind of active site on the silica in order to undergo isomerization. The migration would be slowed down either by reduction in temperature or by the presence of additional pentane molecules on the surface, thus favor-

(6) See, for example, W. Shockley, *Phys. Rev.*, **56**, 317 (1939).

(7) P. W. Levy, *J. Am. Ceramic Soc.*, **43**, 389 (1960).

ing competing modes of decomposition. On the second view, the isomerization would be thought of as a relatively slow unimolecular change arising from some electronically activated state but requiring some additional thermal (vibrational) activation. The activated state would be quenched by the presence of nearby pentane molecules. Reduction in temperature decreases the isobutane yield more than the isopentane yield, indicating that a higher vibrational activation energy is required for isomerization with splitting than for

isomerization without splitting, which seems reasonable.

These attempts to rationalize our observations are of course far from definitive. In fact, practically every change we made in the nature of the solid or the irradiation conditions resulted in some unexpected change in the radiolysis yields. The distribution of products in the radiolysis of an organic compound is certainly far from fixed and can show tremendous variations with apparently minor changes in the molecular environment.

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The Photochemical Decomposition of Acetaldehyde in Aqueous Solutions of Allyl Alcohol at 2537 Å.¹

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RECEIVED AUGUST 30, 1960

The photochemical decomposition of acetaldehyde at 2537 Å. has been studied in aqueous solutions with and without added allyl alcohol in the temperature range from 27 to 73°. The quantum yields of the gaseous products, methane, ethane, carbon monoxide and hydrogen, were determined. The results are consistent with a combination of a free-radical intermolecular reaction and an intramolecular reaction which may be a "geminate" free-radical process.

Introduction

Recent studies in this Laboratory have been directed at obtaining information about photochemical decomposition in aqueous solutions by the use of allyl alcohol as scavenger.^{2,3} In our earlier work on hydrogen peroxide² and acetone,³ the compounds studied were known to undergo photochemical decomposition at 2537 Å. entirely by free-radical mechanisms in the gas phase. In this study the object was to extend our previous investigations to a compound which was known to undergo photolysis in the gas phase by other than a free-radical process.

Acetaldehyde at 3130 Å. decomposes in the gas phase by primary decomposition into free-radicals. At 2804 Å. and shorter wave lengths, two primary photodecompositions occur: the intramolecular formation of methane and carbon monoxide and the formation of methyl and formyl free-radicals.⁴ The most recent study of the photochemistry of acetaldehyde in aqueous solutions⁵ indicated that under radiation from the full light of a mercury arc gaseous products were not formed and that acetaldol is the principal product.

Experimental

The reaction cell, gas train, gas analysis methods and actinometry were similar to those described previously for our acetone studies.³ Hydrogen, which was not previously a product, was oxidized together with carbon monoxide over cupric oxide. The water thereby formed was measured at low pressures in the gas buret.

Light Source.—The helical mercury resonance arc, normally supplied for a.c. operation, was converted to d.c. operation by a half-wave rectification unit capable of supplying 4 kv. With a 20,000 ohm resistance in series with the lamp, the arc current could be stabilized from less than 1 to over 100 mamp.

Reaction Solution.—Acetaldehyde was prepared by the sulfuric acid depolymerization of paraldehyde in a nitrogen atmosphere. The aldehyde was removed by distillation and then redistilled. The middle fraction was retained and stored at Dry Ice temperature over anhydrous calcium sulfate and hydroquinone *in vacuo*. A sample of acetaldehyde of known volume, pressure and temperature was distilled into a known volume of degassed water or allyl alcohol solution at Dry Ice temperature and the initial concentration of acetaldehyde was calculated.

Solution Products.—Quantitative determinations of solution products were not made. However, formaldehyde was found by the use of fuchsin reagent,⁶ and aldol was identified by the use of Dische reagent.⁷

Results

Aqueous Acetaldehyde Photolysis.—Experiments were conducted at three temperatures, 27.6, 49.5 and 73.0°. In Fig. 1 the quantum yields for the gaseous products as a function of temperature for three different intensities are shown. For clarity in representation, the experimental points are not given but, since the same three temperatures were used in all experiments, they occur at both ends of each curve and at the intersection of the straight lines used to connect the experimental points. The concentration of acetaldehyde was 0.05 M for all the experiments shown here. In Fig. 2 the quantum yields for three different acetaldehyde concentrations, 2.9, 7.6 and 24.6 mM, at 73.0° are shown.

Aqueous Acetaldehyde-Allyl Alcohol Photolysis.—The results obtained for solutions of acetaldehyde and allyl alcohol in water at 27.6 and 73.0° are shown in Figs. 3 and 4. It should be noted that the concentration of acetaldehyde and intensity are the same for both temperatures. Within experimental error, hydrogen was not found at either temperature in the presence of even the lowest allyl alcohol concentration used.

(1) Sponsored by the Office of Ordnance Research, U. S. Army.

(2) D. H. Volman and J. C. Chen, *THIS JOURNAL*, **81**, 4141 (1959).

(3) D. H. Volman and L. W. Swanson, *ibid.*, **82**, 4141 (1960).

(4) F. E. Blacet and D. E. Loeffler, *ibid.*, **64**, 893 (1942).

(5) Y. Hirshberg and L. Parkas, *ibid.*, **59**, 2453 (1937).

(6) W. J. Blaedel and F. E. Blacet, *Ind. Eng. Chem., Anal. Ed.*, **13**, 449 (1941).

(7) R. E. Deriaz, M. Stacey, E. G. Teece and L. F. Wiggins, *J. Chem. Soc.*, 1222 (1949).