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The Radiolysis of Organic Solutions. I. Acetone as a Trap for Hydrogen Atoms[1]

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The irradiation with cobalt-60 γ-rays of mixtures of acetone and propanol-2 has shown that addition of acetone is highly effective in reducing the yield of hydrogen from propanol-2, whereas the yields of methane and carbon monoxide are almost unaltered. Irradiation of mixtures of propanol-2 with 5% acetone-d_6 produced methane, 3.2% of which derived from the acetone and hydrogen containing 3.7 atom % deuterium. From these data, from the failure to find biacetyl among the radiolysis products and from the lack of disproportionate increase in the yield of carbon monoxide with addition of acetone, it is concluded that the function of the added acetone is that of a trap for hydrogen atoms rather than that of an energy sink. Comparison of the radiolyses of pure acetone and acetone-d_6 shows that the ratio $G(H_2)/G(D_2)$ is 2.66, the ratio $G(CH_4)/G(CD_4)$ is 1.4 and the ratio $G(CO)_H/G(CO)_D$ is 2.1. Irradiation of equimolar mixtures of acetone and acetone-d_6 gave hydrogen with $H_2/HD/D_2$ ratios, suggesting that about 80% of the hydrogen was formed *via* processes other than unimolecular ones, and a CD_3H/CD_4 ratio of 5.9 (suggesting a thermal radical mechanism for the formation of methane). Evidence for the presence of "hot" hydrogen atoms in the radiolyses of acetone is discussed.

I. Introduction

The use of various additives to react with and remove (scavenge) radicals from a system is a technique long familiar to both radiation chemists[2,3] and photochemists.[4] Typical of such scavengers are iodine, hydrogen iodide, alkyl iodides, triphenylmethyl and diphenylpicrylhydrazyl. Essentially, the action of these scavengers is replacement of an active radical (responsible through further interaction for known final products) with a relatively inactive radical; the net effect upon product formation is to suppress formation of the products characteristic of the active radical (such as methane and ethane from free methyl radical or molecular hydrogen from hydrogen atoms).

Although most of these scavengers appear to be quite effective for removal of alkyl and other complex radicals, their effect on the rate of hydrogen production in systems under irradiation with high energy radiation appears to be slight[2,3] and not clearly, if at all, the result of hydrogen atom scavenging,[2,3] but perhaps of protection through energy transfer or electron capture or even through a spin-orbit interaction.[3] Olefins, however, are known to be effective scavengers for hydrogen atoms.[5,6,8]

This scavenging action probably operates by addition of the hydrogen atoms to the pi-electron system of the olefin. The activation energy for addition of radicals to double bonds is known to be low for gas phase reactions[7] and appears to be low for reactions in the solid phase at 77°K.[6] In gas and liquid phase systems, the immediate result of the initial reaction is often a chain polymerization of the olefin.

The probable nature of this scavenging action suggests that other unsaturated systems should also function as scavengers for hydrogen atoms. Such systems could be ketones, esters, nitriles, aldehydes, thioketones and sulfones, thioesters—in fact, any system containing doubly bonded atoms is naturally eligible for consideration.

From these possibilities we have selected the carbonyl systems—more specifically, ketones—to begin investigation of unsaturated systems in general as scavengers for hydrogen atoms. Carbonyl systems have been chosen because there are several indications in the literature,[8,9] that addition of carbonyl components to ethanol markedly reduced the rate of formation of radiolytic hydrogen. The specific system propanol-2 and acetone was selected for the initial study because the structural similarity both minimized complications and suggested some interesting exchange studies. In addition, propanol-2 is known to be a prolific source of radiolytic hydrogen,[10] which, by analogy with ethanol,[9] should originate principally by a hydrogen atom mechanism.

II. Experimental

Materials.—Propanol-2 was fractionated in a fifty plate column and the heart fraction dried over Drierite. Freedom of the sample from acetone (the impurity of most concern) was established by examination of the infrared spectra of very thick samples and by gas chromatography (which showed a trace of some unidentified impurity). Acetone was similarly purified and its purity similarly established. Acetone-d_6 was obtained from Volk Radio Chemical Co., Chicago; its composition was shown by mass spectra taken at an ionizing voltage of 10.6 volts (nominal) to be acetone-d_6 91.42%, acetone-d_5 7.86% and acetone-d_4 0.72%. The compositions of the various mixtures are reported in volume per cent. (1 volume % acetone = 1.04 mole % = 0.136 *M*).

Irradiations.—Samples of the pure components were distilled into ampules prepared from 11 mm. Pyrex tubing and degassed by the conventional freeze-melt technique. The filled ampules were then sealed off and irradiated in a cobalt-60 source at an intensity of 1.50–1.60 × 10^{18} e.v. per minute per ml. water (ferrous sulfate dosimeter). Samples of the mixture were pipetted directly into the ampules, degassed and sealed.

The ampules were opened in a closed high-vacuum system and the radiolysis gases pumped off through a liquid nitrogen cooled trap with a Toepler pump. These gases noncondensable at 77°K. (hydrogen, methane and carbon monoxide) were collected in a calibrated gas buret (with mercury-calibrated volumes of 0.387, 2.07 and 26.3 ml.) where the STP volumes were measured; they were then pumped into evacuated ampules fitted with stopcocks, from which the analytical samples were collected. Analysis of the gases was accomplished in a modified Consolidated 21-620 mass spectrometer.

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(1) Work performed under AEC Contract AT-(11-1)-GEN-8.

(2) R. H. Schuler, *J. Phys. Chem.*, **62**, 37 (1958).

(3) M. Burton and S. Lipsky, *ibid.*, **61**, 1461 (1957).

(4) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954.

(5) L. M. Dorfman, *J. Phys. Chem.*, **62**, 29 (1958).

(6) R. Klein and M. D. Scheer, *ibid.*, **62**, 1011 (1958).

(7) E. W. R. Steacie, ref. 4, p. 437.

(8) A. S. Newton, THIS JOURNAL, **78**, 4554 (1956).

(9) J. G. Burr, *J. Phys. Chem.*, **61**, 1477 (1957), in the Experimental Section.

(10) W. McDonnell and A. S. Newton, THIS JOURNAL, **76**, 4651 (1954).

Acetone content of several of the mixtures before and after irradiation was determined by infrared spectrometry since acetone is a known radiolysis product of propanol-2.[10]

Evidence for the absence of biacetyl among the radiolysis products of the acetone–propanol-2 mixtures was obtained from (1) the absence of any absorption in the 400 mμ region where biacetyl absorbs strongly and (2) by converting a portion of the mixture to the oxime, dissolving the oxime in water and treating with a water solution of nickel nitrate—no precipitate or color of nickel dimethylglyoxime was observed.

Results

Propanol-2.—The yields of hydrogen, methane and carbon monoxide from the radiolysis of propanol-2 have been measured as a function of specific dose in the range 0.5 to 5 $\times$ 10^{21} e.v./gram. Our value for $G(H_2)$ at a dose of 4 $\times$ 10^{21} e.v./g. is 2.77 which compares well with the value of 2.71 obtained by McDonnell and Newton[16]; but our value for methane, 1.65, invariant with dose, is considerably higher than their value of 1.14. In both investigations, carbon monoxide has been found to be a very minor product. The slope of our $G(H_2)$ line, $\Delta G/(\Delta E \times 10^{-21})$, is 0.071. $G(CO)$ and $G(CH_4)$ were invariant with total dose.

Measurement of the acetone content in several mixtures before and after irradiation showed that the acetone content increased slightly during the radiolysis. The amount of increase was difficult to estimate precisely but appeared to correspond to a G value of between 1 and 2. This value must represent a balance between consumption of acetone by the hydrogen trapping process and formation of acetone by propanol-2 radiolysis (with a reported[10] G of 2.96). Thus, the consumption of acetone by the hydrogen trapping must occur with a G of not more than 1–2 also (conforming rather well to the observed decrease in $G(H_2)$). The high G value pinacol-forming reaction which has been observed in irradiated benzophenone-propanol-2 solutions (to be reported in a forthcoming paper) is, of course, not observable in these solutions of acetone and propanol-2.

Acetone and Acetone-d_6.—The yields of hydrogen, methane and carbon monoxide from the radiolysis of acetone are shown in Fig. 1. $G(H_2)$ appears to be dose-independent: this is understandable since the concentration of carbonyl group remains essentially constant. The dose-dependencies of methane and carbon monoxide are important but do not have any immediately apparent interpretation.

A comparison of the radiolysis of acetone with that of acetone-d_6 is shown in Table I.[11] (The dose in each case was 1.5 $\times$ 10^{21} e. v./g.)

TABLE I

RADIOLYSES OF ACETONE AND ACETONE-d_6

	Acetone	Acetone-d_6[c]
$G(H_2, D_2)$	0.98	0.36[a] $\pm$ 0.01
$G(CH_4, CD_4)$	1.80	1.29[b] $\pm$ 0.02
$G(CO)$	0.55	0.25 $\pm$ 0.01
G(gas)	3.30	1.97

[a] The deuterium fraction contained 2.5% HD. [b] The methane fraction includes 6.9% CD_3H. [c] The values are the averages of duplicate experiments.

Data obtained from the irradiation of equal volume mixtures of acetone and acetone-d_6 are shown in Table II.

TABLE II

RADIOLYSES OF MIXTURES OF ACETONE AND ACETONF-d_6

Run no.	G-(gas)	% composition of gas								
		H_2	HD	D_2	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	CO
1[a]	3.03	11.1	7.5	2.5	31.9	2.7	0.5	20.6	3.3	20.0
2[b]	2.90	10.9	7.5	2.8	31.1	3.1	0.0	21.3	3.9	19.5

[a] Air-free and water-free basis; the mass spectrometer sample contained 7.5% water and 0.5% air. [b] Air-free, water-free basis; the mass spectrometer sample contained 6.8% water and 0.3% air.

Mixtures of Propanol-2 with Acetone and with Acetone-d_6.—The yields of hydrogen, methane and carbon monoxide during the radiolyses of various mixtures of propanol-2 and acetone are shown on Figs. 2 and 3. The dose-dependency of yield of total non-condensable gases for several of these mixtures was studied as a function of dose. A slight and variable dose dependency was evident; the trend was not sufficiently consistent to warrant the usual extrapolation to zero dose. The data shown in Figs. 2 and 3 have therefore all been normalized to a dose of 1.0 $\times$ 10^{21} e.v./g.; this is the dose at which most of the experiments were run.

Figure 2 shows the dependency of $G(H_2)$, $G(CH_4)$ and $G(CO)$ upon acetone concentration for the whole range of acetone concentration from 0–100%. The region from 0–5% acetone concentration is shown with an expanded scale in Fig. 3.

The composition of the gas obtained during the radiolyses of mixtures of propanol-2 with 5 volume % of acetone-d_6 is shown in Table III.

TABLE III

RADIOLYSES OF MIXTURES OF PROPANOL WITH 5% ACETONE-d_6

Run no.	G-(gas)	% composition of gas								
		H_2	HD	D_2	CH_4	CH_3D	CH_2D_2	CHD_3	CD_4	CO
1	3.91	47.9	1.62	0.05	46.0	2.4	0.4	1.1	0.1	0.43
2	3.90	45.5	1.7	.08	46.0	2.2	1.70	1.2	.2	1.4
3	3.88	47.3	1.7	.1	45.1	2.5	0.6	1.1	.1	1.1

Discussion

It is apparent that the addition of acetone to propanol-2 in quantities as low as 0.1% (0.014 M) measurably depresses the yield of hydrogen from propanol-2, whereas the yield of methane is independent of acetone content and the rate of carbon monoxide formation is very nearly that to be expected of a non-interacting pair of substances.

Data similar to those reported here for mixtures of propanol-2 and acetone have been obtained for cyclohexane–benzene,[12] cyclohexane–benzene-d_6[13]

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[11] P. Ausloos, University of Rochester, personal communication, has informed us of similar experiments carried out on acetone, acetone-d_6 and equimolar mixtures of these two. The Rochester values for $G(H_2, D_2)$, $G(CH_4, CD_4)$, $G(CO)$, respectively, for acetone and acetone-d_6 are 0.87, 0.42; 2.58, 2.34; 0.83, 0.64. We believe, in view of the dose dependency we observed for the $G(CH_4)$ and $G(CO)$ values, that these differences reflect in part a dependency on total dose and, in part, a dependency on dose rate of the two sets of experiments. Our cobalt source has a very high dose intensity of 1.4 $\times$ 10^{15} e.v./ml. water-min. in the central region. Our results agree quite well with those of the Rochester group with regard to the distribution of isotopic methanes and isotopic hydrogen species among the products of the mixture irradiations. We are happy to agree thoroughly with their conclusions regarding the mechanisms of methane formation from acetone. ADDED IN PROOF.—The article has now appeared: THIS JOURNAL, **80**, 5171 (1958).

[12] J. P. Manion and M. Burton, *J. Phys. Chem.*, **56**, 560 (1952).

[13] M. Burton and W. N. Patrick, *ibid.*, **58**, 421 (1954).

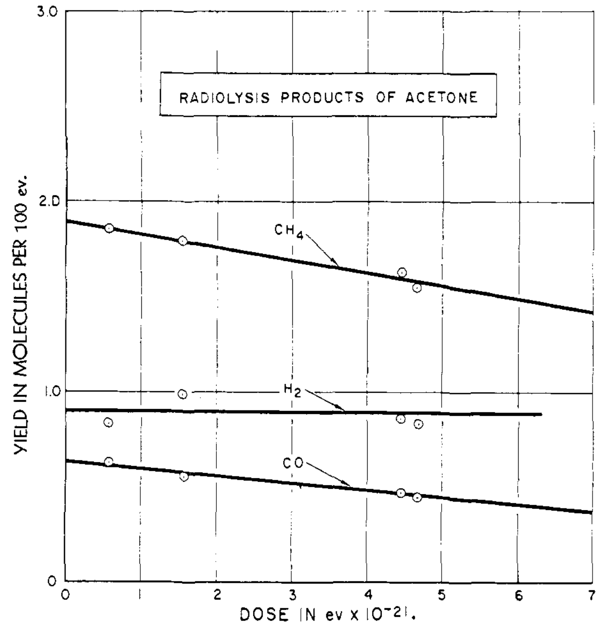

Fig. 1.

and propionaldehyde–benzene-d_6,[14] as well as for ethane–propylene.[5] It was found that addition of benzene or benzene-d_6 to cyclohexane or propionaldehyde depressed $G(H_2)$ for the substrate material and that addition of propylene depressed the yield of radiolytic hydrogen from ethane.

The depressant effect of such unsaturated additives upon the rate of hydrogen formation is usually discussed in terms of two processes, which can be competitive. One of these is energy (excitation or ionization) transfer from the excited or ionized substrate molecules[15]; the other is the scavenger action of the unsaturated substance for hydrogen atoms. In the case of mixtures of acetone and propanol-2, both processes must be considered. Examples have been cited above to show that unsaturated substances are scavengers for hydrogen atoms. Both excitation transfer and ionization transfer from propanol-2 to acetone are energetically feasible since the ionization potential of acetone is 9.92 e.v.[16] and that of propanol-2 is 10.27 e.v.[17] Propanol-2, like other alcohols, is transparent above 2000 Å. and acetone has a strong transition at about 2900 Å.

Energy Transfer.—In principle energy transfer from a substrate molecule, such as propanol-2 or cyclohexane, to a solute molecule, such as acetone or benzene, should result in disproportionate decomposition of the solute molecule since it receives energy both directly from the incident radiation and indirectly from substrate molecules. By this criterion, Patrick and Burton consider that energy is transferred from benzene to propionaldehyde[14] *i.e.*, benzene sensitizes the decomposition of propionaldehyde. This criterion was not applied to mixtures of benzene and cyclohexane because the

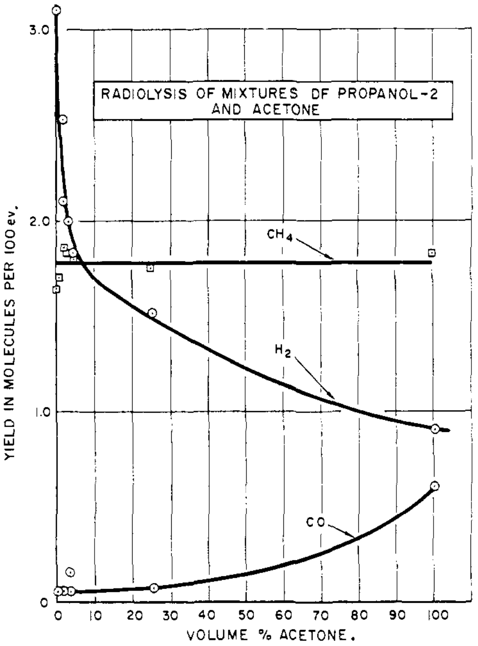

Fig. 2.

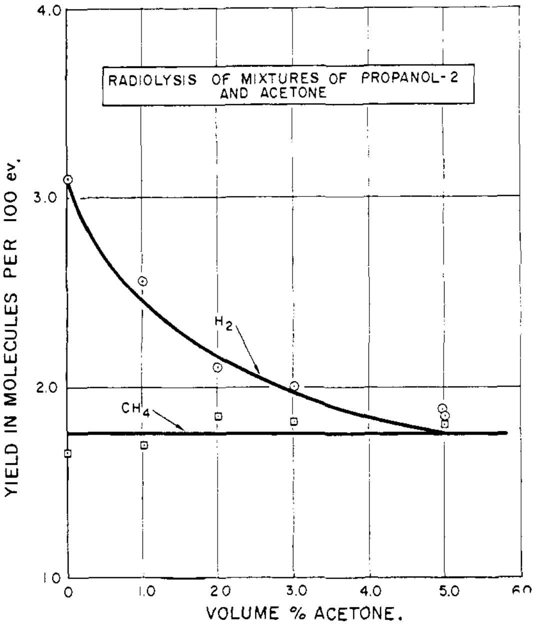

Fig. 3.

yield of gaseous radiolysis products from benzene is so low that it was considered to be essentially inert to radiation in the mixtures under examination.

It is worth considering the effect of energy transfer upon the product yields in more detail, for the acetone–propanol-2 system. The energy transferred to the acetone molecule could put it into the electronic state whose decomposition produces the radiolysis products reported here—hydrogen, methane and carbon monoxide. In this case, an enhanced yield of these products would be expected. The transferred energy could possibly put the acetone molecule into the electronic state and circumstances responsible for product formation observed in the gas-phase photolysis of acetone[4]–methane,

[14] W. N. Patrick and M. Burton, *J. Phys. Chem.*, **58**, 424 (1954).

[15] M. Burton and S. Lipsky, *ibid.*, **61**, 1461 (1957).

[16] J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

[17] I. Omura, H. Baba and K. Higasi, *Bull. Chem. Soc. Japan*, **28**, 147 (1955).

ethane, carbon monoxide and biacetyl. In this case we should expect to see an enhanced yield of methane and carbon monoxide. However, it is known[18,19] that the yields of gaseous products from the photolysis of liquid acetone are much lower than the yields observed from the photolysis of gaseous acetone so if the transferred energy were to put the condensed phase acetone into the photo-chemical excited state, then no enhancement of gas yields would probably be observable. In all of these cases, however, energy transfer should result in a decreased over-all decomposition of the propanol-2, *i.e.*, not only should addition of acetone decrease the yield of hydrogen formation but it should also decrease the yield of methane from the propanol-2.

Application of these concepts to the data presented in this paper leads to the definite conclusion that in this case the solute acetone is functioning primarily as a scavenger for the hydrogen atoms rather than as an energy sink. From the data in Fig. 3, addition of acetone to propanol-2 does not result in an enhancement of carbon monoxide formation. Biacetyl, another possible radiolysis product of acetone, could not be detected among the radiolysis products. Hydrogen and methane are radiolysis products of both acetone and propanol-2, and the data presented in Figs. 2 and 3 do not enable one to determine the origins of these two products in the mixture. However, use of acetone-d_6 rather than acetone in the mixture does allow one to determine which parts of the methane and hydrogen originate in the solute acetone.

At an acetone-d_6 content of 5 volume % (where $G(H_2)$ has dropped from 3.0 to 1.9, and where the invariant yield of methane is still 1.8), reference to Table III shows that the methane produced by radiolysis of this mixture contains 96.8% of methane with CH_3 units (thus deriving from the propanol-2) and 3.2% of methane with CD_3 units (thus deriving from the acetone). If the decomposition rates of the individual components are unaffected by the mixing (*i.e.*, in the absence of energy transfer), then one would expect that the methane would originate from each component in proportion to the absorption of energy by each (*i.e.*, in proportion to the electron fraction of each component) or very nearly in the ratio 96/4. The value of this ratio observed in the actual experiment, 96.8/3.2, is close to this expected value. While we are not sufficiently certain of the mass spectrometer accuracy to say whether the slight deviation from the 96/4 ratio indicates a desensitization of acetone decomposition by the propanol-2, it is, at least, apparent that the presence of propanol-2 does not substantially enhance the decomposition of the acetone.

It is more difficult to draw conclusions from the deuterium content of the hydrogen, since this deuterium does not clearly all originate from decomposition of acetone molecules but may also reflect the bi-molecular reactions of species originating from the propanol-2. However, the total yield of deuterium from this mixture (namely, hydrogen originating by all processes from the acetone) is 0.016; the value which might be expected from 5 volume % acetone would be 0.05 × 0.36 = 0.015. This agreement suggests also, although more indirectly, that the presence of propanol-2 does not enhance the decomposition of the acetone.

Thus, the yields of carbon monoxide, methane and hydrogen from the propanol-2 and acetone mixtures all suggest that the two components are decomposing at rates which are in close agreement with those to be expected from their electron fraction in the mixture. The absence of any biacetyl among the radiolysis products suggests that the presence of the propanol-2 has not effected a change in the nature of the acetone decomposition. For these reasons it does not seem probable, therefore, that energy transfer from propanol-2 to acetone can be responsible for the effect of solute acetone upon the yield of radiolytic hydrogen from propanol-2.

Additional information about the nature of this scavenger action may be gained by considering the shape of the hydrogen curve in Fig. 2. Over the whole middle range, the shape of this curve is that of a simple kinetic competition (equation 1, where $G^0 = G(H_2)$ from pure isopropyl alcohol and $G_\infty = G(H_2)$ from pure acetone), and $K = 10\text{–}11$.

$$\frac{G^0_{H_2} - G_{H_2}}{G_{H_2} - G_{H_2}{}^\infty} \times \frac{1}{[Me_2CO]} = K \qquad (1)$$

The value of K rises sharply at both very low and very high concentrations of acetone. The approximate nature of this relationship may be caused by the formation in the radiolysis of unscavengable ("hot") hydrogen atoms, for which evidence will be presented below. This relationship can be considered in terms of a competition between hydrogen atom abstraction and hydrogen atom addition to acetone.

$$H + RH \longrightarrow H_2 + \text{Residue}_1 \qquad (2)$$

$$H + CH_3COCH_3 \longrightarrow \text{Residue}_2 \qquad (3)$$

It is convenient to think of these as the competitive reactions because such a competition can explain why acetone is such a relatively inefficient scavenger. Scavenging of alkyl radicals by iodine, or of H and OH radicals in the radiolysis of water by metal ions, is complete at scavenger concentrations of 10^{-4} *M;* the scavenging action of acetone for hydrogen atoms only begins to be appreciable at concentrations of 10^{-2} *M* and more. The latter range of effective concentration is also observed in far scavenger benzene or olefin in similar systems. It is probable that in the case of the sort of scavenging discussed in this paper we are observing a competition between two processes whose rate constants are relatively close together, in contrast to the scavenging action of iodine for alkyl radicals where the competition is between two reactions (alkyl radical abstraction *versus* reaction with iodine molecules) of widely different rate constants. The scavenging reaction of acetone only begins to compete effectively with abstraction at relatively high concentrations of acetone.[20]

The Radiolysis of Acetone.—The evidence presented above for the ability of acetone to scavenge

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(18) R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955).

(19) J. P. McNesby and A. S. Gordon, THIS JOURNAL, **76**, 1416 (1954).

(20) It is interesting to note that the scavenging action of acetone for hydrogen atoms was first suggested by Fricke, Hart and Smith (*J. Chem. Phys.*, **6**, 229 (1938)) in a study of the radiolysis of aqueous acetone by X-rays.

hydrogen atoms raised further questions. One of these concerned the mechanism by which hydrogen is formed in the radiolysis of pure acetone. In view of the efficient scavenging action of acetone for hydrogen atoms, it seemed possible that this radiolytic hydrogen might represent a residual molecular process for hydrogen formation (which, of course, would not be affected by a scavenger).

Answers to this question were sought by examining the radiolysis of acetone-d_6 and equimolar mixtures of acetone and acetone-d_6. The results of these investigations are shown in Tables I and II.

If the radiolytic hydrogen from acetone were to be formed entirely by a residual "molecular" process, then the hydrogen from the mixture should contain only H_2 and D_2, but no HD (except that produced by γ-ray-induced equilibration of the hydrogen present in the gas space above the liquid; this is expected to be small because the large concentration of acetone molecules in this phase should prevent the usual chain equilibration reaction). Inspection of Table II shows that this is not the case; the hydrogen contains a fraction of HD which corresponds to a value of $(HD)^2/(H_2)(D_2) = 1.85$.[21]

The production of HD in the acetone–acetone-d_6 mixture is quite in contrast to the experience of Dorfman[5] who found that addition of 10–15% of gaseous ethylene or propylene to a gaseous ethane–ethane-d_6 mixture reduced HD production substantially to zero.

It is evident that some HD-forming reaction is a prominent contributor to the processes reponsible for hydrogen evolution in this mixture. Owing to the evidence presented above for the scavenging power of acetone for hydrogen atoms, we do not believe that thermal hydrogen atoms can be responsible for the formation of HD. Other possibilities are hydrogen atoms with sufficient kinetic energy ("hot" hydrogen atoms) that reaction occurs within the first few collisions (whence abstraction should be preferred process owing to the larger concentration of C–H bonds than carbonyl double bonds) or bi-molecular processes which do not involve hydrogen atoms.

A potential clue to the processes occurring in the acetone–acetone-d_6 system probably lies in the observation that $G(H_2)/G(D_2)$ for the separated components is 2.72, whereas $G(H_2)/G(D_2)$ from the equimolar mixture is 4.0, and $G(H)/G(D)$[22] is 2.28. However, to test the plausibility of hydrogen atom processes in this system, we must consider isotope effects in formation of molecular hydrogen and deuterium, in formation of possible H and D atoms, in the addition reactions of these H and D atoms and in the abstraction reactions of these H and D atoms. A complete analysis is impractical since we have no values for the individual isotope effects. Manipulation of the above numbers, using several different sets of assumptions, made it apparent that at least we could not exclude the participation of hydrogen atoms on the basis of these several isotope effects.

We do believe, however, that since the over-all isotope effect is different for the mixture than it is for the separated components (we believe this difference to be real since we have observed a similar difference for the toluene–toluene-d_8 and biphenyl–biphenyl-d_{10} systems), that bimolecular reactions either involving hot hydrogen atoms, ion-molecule, or excited molecule–molecule reactions are important in the radiolysis of acetone.

Table II also supplied evidence regarding the mechanism of methane formation. The thermal decomposition of gaseous mixtures of acetone and acetone-d_6[23] and the photochemical decomposition of liquid mixtures of acetone and acetone-d_6[24] are commonly believed to produce methane *via* a radical mechanism. In all of these studies, the ratio CD_3H/CD_4 has been observed to be about 6–7 at temperatures of 55–150°; in pyrolysis, this ratio decreases with increasing temperature[22] and in liquid photolysis, the ratio decreases with decreasing temperature. The corresponding ratio found in our radiolysis (Table II) is 5.9, *i.e.*, the relative yields of CD_3H and CD_4 are characteristic of H and D abstraction by a thermal CD_3 radical. Another measure of this isotope effect characteristic of this radical reaction is the ratio $CH_4 + CD_3H/(CD_4 + CH_3D)$, which for a radical reaction can be computed to be about 12.8[23] and for a disproportionation-type (molecular) process to be 1.0. The value found for the radiolysis is about 8.2 (very sensitive to minor errors in analysis since both values in the denominator are quite small), so this is clearly more characteristic of a thermal radical reaction than a molecular process. The sort of values observed in a reaction where methane is formed largely by a molecular process have been reported by Dorfman.[5]

Comparison of Radiolysis Data with Mass Spectral Data.—Comparison of radiolysis mechanisms with processes found to occur in the mass spectrometer has been made in a previous paper,[25] and the correlations discussed there are found to hold in the case of acetone also. The radiolysis data suggest that methane is formed *via* methyl radicals. In the mass spectra,[26] the ratio of the peak at m/e 43 (radical process) to that at m/e 42 (molecular process) is 15–16—indicating that dissociation of acetone by electron impact on the dilute gas phase also produces predominantly CH_3 fragments. The size of the hydrogen loss peaks in the acetone patterns are too small to give definite information.

Acknowledgments.—We are indebted to R. A. Meyer for the mass spectrometer analyses: to D. E. McKenzie and J. P. Howe for many helpful discussions during preparation of this communication.

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[21] If the fraction of "molecular" process is computed by the expression reported by Dorfman (*J. Phys. Chem.*, **60**, 826 (1956)), this fraction is $x \geqq 0.21$.

[22] Namely, the ratio of total hydrogen atoms to total deuterium atoms in the radiolytic hydrogen from the mixture.

[23] J. P. McNesby and A. S. Gordon, This Journal, **76**, 1416 (1954); J. P. McNesby, T. W. Davis and A. S. Gordon, *ibid.*, **76**, 824 (1954).

[24] R. Pieck and E. W. R. Steacie, *Can. J. Chem.*, **33**, 1304 (1955).

[25] J. G. Burr, *J. Phys. Chem.*, **61**, 1483 (1957).

[26] F. E. Condon, This Journal, **73**, 4675 (1951).