

The Use of Deutero Compounds as Indicators for the Presence of Free Radicals in Organic Decomposition Reactions

E. W. R. Steacie and W. A. Alexander

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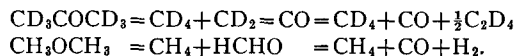


The Use of Deutero Compounds as Indicators for the Presence of Free Radicals in Organic Decomposition Reactions

There is at present considerable uncertainty regarding the importance of free radicals in organic decomposition reactions. Information on this point is particularly desirable in the case of substances which decompose by a first-order mechanism. It is certain that radicals do participate in decomposition processes at high temperatures, and that they can often exert a sensitizing effect on other reactions. It also seems certain, however, that the predictions of the free radical chain theory regarding stationary concentrations of atoms and radicals, and the activation energies of elementary processes are frequently definitely in disagreement with the facts. It is therefore desirable to have as many independent methods of investigating the question as possible.

We have recently carried out experiments in which a mixture of two organic compounds is decomposed. In one of the compounds all the hydrogen atoms have been replaced by deuterium. If decomposition occurs by a molecular mechanism, the products of the decomposition of one compound should be entirely "light," and those of the other entirely "heavy." If, however, free radicals or atoms intervene, then cross products will be formed. It should therefore be possible to obtain considerable information concerning the mechanism of the decomposition from an examination of the deuterium distribution among the products.

Thus mixtures of deutero-acetone and ordinary dimethyl ether have been decomposed at 590°C. The general course of the decompositions is known to be



It follows, therefore, that the hydrogen from the products should be all light if the process goes as indicated. If, however, formaldehyde decomposes by $\text{HCHO} = \text{H} + \text{CHO}$, then the resulting hydrogen atom is as likely to extract another atom from the ether as from acetone, so that there should be approximately equal chances of getting HD and H_2 . Hence, on a radical mechanism, we would expect the hydrogen to be approximately 25 percent heavy.

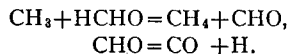
The actual investigation is complicated by the fact that hydrogen from the decomposition of methyl ether will slowly exchange with the products of the acetone decomposition. This effect, however, is not great if short contact times are used, and can be corrected for by blank experiments. The result found is that within an experimental error of about 2 percent the hydrogen from the mixture decomposition is entirely light.

Thus in a number of experiments a mixture of acetone (48.3 percent heavy) and methyl ether was heated at 590°C for 5 minutes and then withdrawn and the hydrogen separated and analyzed. The mean deuterium content found was 3.3 percent. In blank experiments acetone and ether were decomposed separately, and the products were mixed and heated to 590°C for 5 minutes. The mean

deuterium content of the hydrogen in this case was 2.1 percent.

It may therefore be concluded that formaldehyde does not decompose by a free radical mechanism, since it is very unlikely that the reaction $\text{H} + \text{CD}_3\text{COCOD}_3 = \text{HD} + \text{CD}_2\text{COCOD}_3$ should have a very much slower rate than that of $\text{H} + \text{CH}_3\text{OCH}_3 = \text{H}_2 + \text{CH}_3\text{OCH}_2$. Indeed Rice estimates the former to be the faster, and in any case it appears probable that reactions of this type have very low activation energies, and hence collision yields not far from unity at 590°. This is in agreement with the results of Patat and Sachsse¹ who found a negligibly small stationary H atom concentration during the decomposition of formaldehyde.

Fletcher and Rollefson² have pointed out that formaldehyde formed as an intermediate in the decomposition of methyl ether itself decomposes about 15 times faster than normal. They suggest that this is due to a sensitized decomposition by methyl radicals from the ether decomposition, *viz.*



Since this would also involve the occurrence of free H atoms, our experiments cast considerable doubt on this explanation.

Our results also seem to preclude the possibility of a very high concentration of methyl radicals during the methyl ether decomposition, since otherwise the reaction $\text{CH}_3 + \text{H}_2 = \text{CH}_4 + \text{H}$ would be expected to come into play.

It is, of course, too early to draw sweeping conclusions from the results, but the method seems to have possibilities. The work is being continued with more accurate analytical methods.

This work has been done with financial assistance from the National Research Council of Canada, and one of us (W. A. A.) wishes to acknowledge the receipt of a Bursary from the same source.

E. W. R. STEACIE
W. A. ALEXANDER

Physical Chemistry Laboratory,
McGill University,
Montreal, Canada.

¹ Nach. Ges. Wiss. Göttingen **1**, 41 (1935).

² J. Am. Chem. Soc. **58**, 2129 (1936).

Effect of CS₂ as Solvent On Electric Moment of Solute

In a recent article¹ the writer reported data from measurements of the polarization of ethyl alcohol in extremely dilute solutions using benzol and carbon tetrachloride as solvents. It was reported that measurements had been made on solutions of ethyl alcohol dissolved in carbon disulfide but the polarization of the alcohol as obtained from these solutions was not reported because of slight deviations of the P_2C_2 versus C_2 curve from linearity which were attributed to some possible chemical reaction between the carbon disulfide and the brass condenser. The electric moment of alcohol was not calculated from these data.

Recently the writer received a private communication from K. Higasi who stated that he had measured the polarization of isopropyl and isobutyl alcohol in carbon disulfide and had obtained values of electric moment equal to 1.41 and 1.48 (times 10^{-18} e.s.u.), respectively, which did not compare favorably with values of μ equal to 1.70 times 10^{-18} e.s.u. for both substances obtained by him² from data on benzol solutions.

Using the previously mentioned unreported data on twenty-eight solutions of ethyl alcohol in carbon disulfide ranging in concentration from 0.0045 to 0.9 mole percent the writer has obtained values of electric moment of ethyl alcohol of μ equals 1.51 times 10^{-18} e.s.u. from solutions in which specially purified carbon disulfide was used, and μ equals 1.55 times 10^{-18} e.s.u. from solutions in which the carbon disulfide was not specially purified by the writer. These values must be compared with μ equals 1.70 times 10^{-18} e.s.u. from benzol solution and μ equals 1.67 times 10^{-18} e.s.u. from carbon tetrachloride solution.

Thus the values μ as obtained from carbon disulfide solutions were low by approximately the same amount in both of the above cases, but the discrepancies obviously cannot be attributed to chemical reaction between the material of the condenser and the solvent since Higasi reports the use of a platinum condenser. It seems impossible to attribute the low value to the presence of an impurity such as water vapor since it is believed to have been completely removed by the writer from the specially purified reagent which gave the lower value of μ .

The writer now has under construction a completely new set of apparatus with which it is hoped to attain even greater precision of measurements for the investigation of this effect.

FRANK E. HOECKER

Department of Physics,
University of Kansas City,
Kansas City, Missouri,
March 22, 1937.

¹ J. Chem. Phys. **4**, 431 (1936).

² Sc. Pap. I. P. C. R. **28**, 284 (1936).