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Isotopic Labelling Studies in Irradiated Organic Solutions

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ABSTRACT

Non-linear interactions between solvent and solute are observed in the radiolysis of binary organic mixtures. The use of labelled molecules to diagnose both the nature of the excited solvent species and also the nature of the interaction between these excited secties and the solute molecules will be described.

The particular systems discussed in detail will be: 1. cyclohexane + ^{14}C-benzene; 2. tritiated cyclohexane + ^{14}C-benzene; 3. tritiated cyclohexane + benzoquinone; 4. tritiated cyclohexane + cyclopentene; 5. cyclohexane + ^{14}C-cyclohexene; 6. cyclohexane or cyclohexane d_{12} + benzene or benzene-d_6; 7. cyclohexane-d_{12} + cyclopentane; 8. various mixture of cyclohexane, cyclopentane and deuterated analogs with corresponding olefins and the deuterated olefins; 9. mixtures of light and heavy water vapor with cyclopentane, methane, cyclohexane and other hydrocarbons.

Analysis of the products obtained in the irradiation of these systems has been informative about the nature of the quenching and scavenging processes wich take place and also about the nature of the, reactive species involved.

The nature of the reaction processes arising from the action of ionizing radiation in organic systems is recognized as extremely complex. Direct observations of the existence and the reactions of free radical and ionic intermediates have been achieved by spectrometric techniques. However, a complete understanding of the chemical significance of such intermediates is reached only by detailed examinations of the effects of varying experimental environments. We have endeavored to elucidate the radiation induced reaction processes in organic mixtures by studies of the product yield variations as functions of the solute concentrations. Due to the complexity of a large number of intermediates, however, it is often impossible to derive unequivocal correlations between the observable product yields and the probable reaction processes (1). Therefore, we have resorted largely to isotopic labelling techniques which can effect an increase in information both by an increase in the number of observable products (2) and by meaningful shifts in product distributions.

In order to minimize the difficulties involved, we have restricted ourselves to systems where only relatively small numbers of significant products are formed. In the radiolysis of liquid cyclohexane, only hydrogen, cyclohexane and bicyclohexyl are formed in major yields. The apparent selectivity in the modes of decomposition of the reactive intermediates belies the complex physical and chemical processes involved in the radiolytic reaction. In a simplified representation, cyclohexane decomposition is accounted for by the following series of reactions.

$$C_6H_{12} \rightarrow C_6H_{12}^* \; (C_6H_{12}^+ + e) \qquad (1)$$

$$C_6H_{12}^* \; (C_6H_{12}^+ + e) \rightarrow C_6H_{10} + H_2 \qquad (2)$$

$$C_6H_{12}^* \; (C_6H_{12}^+ + e) \rightarrow C_6H_{11} + H \qquad (3)$$

$$H + C_6H_{12} \rightarrow H_2 + C_6H_{11} \qquad (4)$$

$$C_6H_{11} + C_6H_{11} \rightarrow C_6H_{10} + C_6H_{12} \qquad (5)$$

$$C_6H_{11} + C_6H_{11} \rightarrow C_{12}H_{22} \qquad (6)$$

The nature and the formation of the excited cyclohexane intermediate in reaction (1) is rather complex and its transient existence is indicated by the solvent-solute interactions observed in the radiolysis of parafin-olefin solutions.

The effect of benzene in reducing product yields from cyclohexane can be considered to result from several possible types of interactions :

(1) hydrogen atoms and/or cyclohexyl radicals may be scavenged by addition to the benzene,

(2) excited cyclohexane may be deactivated by energy or charge transfer to benzene,

(3) electrons produced in the initial ionization may be scavenged by addition to benzene thus converting the $e + C_6H_{12}^+$ recombination to $C_6H_6^- + C_6H_{12}^+$ recombination which may not result in cyclohexane decomposition.

We have studied the isotopic hydrogen yields in C_6H_{12}- C_6H_6, C_6H_{12}-C_6D_6, C_6D_{12}- C_6H_6 and C_6D_{12}- C_6D_6 mixtures (3). At low benzene concentrations, the effect on the hydrogen yield is much more pronounced when the cyclohexane is deuterated; however, as the benzene content is increased, the overall effect appears to depend rather on whether the solute is deuterated. Obviously, the observed results cannot be accounted for by any one of the above processes, and complex modes of interactions are definitely indicated.

In order to establish the benzene consumption as well as the fate of the benzene consumed, we have resorted to the tracer technique with the use of ^{14}C-benzene as the solute (4). Benzene loss in irradiated cyclohexane-benzene solutions was measured by gas-chromatography, and it was found to be a linear function of the square root of the benzene concentration. The benzene consumed, as measured by the carbon-14 activity, was found to appear mainly in the dimer and higher molecular weight products. The nature of the interaction leading to formation of the benzene-containing higher molecular weight products was further investigated by using mixtures composed not only of ^{14}C-benzene but also tritiated cyclohexane. The polymer obtained by irradiations of such mixtures is labeled with both carbon-14 and tritium (5). The benzene content can be calculated from the carbon-14 activity, and thus the cyclohexane content by difference. Having first determined that the polymer from cyclohexane (t) alone is not appreciably enriched in tritium, we can conclude that an excess tritium activity observed in the polymer from the mixture is associated with the benzene moiety. These experiments demonstrated that hydrogen atoms are scavenged by either benzene or a benzene intermediate arising from interactions with irradiated cyclohexane.

Another highly significant observation in the radiolysis of tritiated cyclohexane-^{14}C-benzene mixtures is that the tritium activity associated with the benzene moiety is very large. These results can be explained only by an abnormal isotope effect favoring tritium over hydrogen atom addition to the benzene or benzene-containing intermediates. Such an isotope effect is observable only in high energy radiation induced reactions where only a small normal isotope effect may be involved in the bond breaking process leading to H and T atom formations. The subsequent fate of the H and T atoms in paraffin-olefin mixtures may be represented simply by reactions (7) and (8),

$$\mathrm{H,T + HR \rightarrow H_2, HT + R} \tag{7}$$

$$\mathrm{H,T + S \rightarrow HS, TS} \tag{8}$$

where HR represents a saturated hydrocarbon and S represents an unsaturated scavenger. The relative yield of the tritium-containing radical is given in equation (9).

$$\frac{\mathrm{G\,(TS)}}{\mathrm{G\,(HS)}} = \mathrm{G(T)}\left[1 + \frac{k_7^h\,\mathrm{(HR)}}{k_8^h\ \mathrm{(S)}}\right] \Big/ \mathrm{G(H)}\left[1 + \frac{k_7^t\,\mathrm{(HR)}}{k_8^t\ \mathrm{(S)}}\right] \tag{9}$$

The isotope effect in the abstraction reaction (7) is usually small, and so at low olefin concentrations the above equation is reduced to

$$\frac{\mathrm{G\,(TS)}}{\mathrm{G\,(HS)}} = \frac{\mathrm{G\,(T)}\,k_8^t}{\mathrm{G(H)}\,k_8^h} \tag{10}$$

The isotope effect for the initial hydrogen atom formation, G(H)/G(T) has been measured as 1.7 in the radiolysis of water vapor (6). A similar value may be expected in hydrocarbon radiolysis. Thus, the ratio G(TS)/G(HS) would be larger than unity, when the rate constant ratio k_8^t/k_8^h is greater than about two.

Since the G (TS)/G (HS) ratio can be established only from the tritium activities in the stable products resulting from these radicals, a complete mechanistic understanding of the reaction system is highly essential. Since it is difficult to characterize the polymeric product, the G (TS)/G (HS) ratio cannot be estimated for cyclohexane-benzene solutions. We have, therefore turned our attention to systems with mono-olefins as the solutes (7), where the intermediate radicals may be expected to react mainly by disproportionation and recombination processes. With cyclopentene as the scavenger, for example, cyclopentyl radicals are formed by H or T atom additions and these radicals will react further to result in cyclopentane, bicyclopentyl and other mixed dimers. A necessary precaution, therefore, is to find conditions under which one or more of these products are not formed by other competing processes.

In our studies of the reaction processes in the radiolysis of paraffin-olefin solutions, again we found the isotope labelling technique a useful tool. In the radiolysis of 1 % ^{14}C-cyclohexene in cyclohexane (7), it was observed by Cher and co-workers that the product mixtures can be accounted for almost entirely by hydrogen atom scavenging reactions. However, we cannot ignore mounting evidences in support of energy or charge transfer processes. In particular, Ausloos and co-workers (9) have shown that cyclopentane may be formed by H_2-transfer from cyclohexane ion to cyclopentene. We have irradiated various binary combinations of cyclohexane, cyclohexene, cyclopentane, cyclopentene mixtures (10, 11), and measured the product yields as functions of the olefin concentration and as effect of deuterium substitutions in the solvent or solute molecules. The results indicate that at low olefin contents the interactions are due largely to radical scavenging processes, but at high olefin concentrations, physical interactions become predominant. The latter processes apparently lead mainly to diolefinic dimers as the products, and these were attributed to reactions involving ionic intermediates.

In view of these observations, it is clear that the hydrogen atom scavenging reaction should be studied at low olefin contents and only the corresponding dimer may be considered as a reasonably specific product to result from subsequent reactions of the radical intermediate. In addition, radical transfer reactions should be minimized by irradiations at low temperatures. Our preliminary studies (7) of the abnormal isotope effect for hydrogen atom addition to olefins are definitive, but the relative values derived for T atom and H atom additions are subjected to errors arising from our failure to consider all possible complications. More reliable investigations shall be carried out following studies to determine the optimum conditions.

Thus far we have described only the applications of the isotope labelling technique in the radiolysis of hydrocarbon mixtures. Currently, we are investigating the isopropanol-acetone system, in which the solvent and the solute molecules possess identical carbon-oxygen skeletons. Hydrogen atom scavenging by acetone is well established (12), and the resulting semipinacol radical, Me_2COH, may arise also by the loss of a hydrogen atom from isopropanol. The origins and subsequent reactions of this radical are studied by carbon-14 labelling either in isopropanol or in acetone (13). The data for the acetone-isopropanol conversion fit a skewed second order relationship, G (acetone-isopropanol) $= k(A)(I) + 0.4(A)$, where (A) and (I) are, respectively, ^{14}C-acetone and isopropanol concentrations and $k = 29.3$. Similarly, with carbon-14 labelling in the isopropanol, G(isopropanol-acetone) $= 14.7(A)(I) + 1.85(I)$. Although the mechanisms for these interconversions are not yet fully understood, we can conclude that efficient sharing of the energy absorbed by either component must be involved. We believe that the positive isopropanol ion and the negative acetone ion are the key intermediates.

We have described rather briefly the applications of the isotope labelling technique to radiolytic studies in organic systems. Due to space limitations we have limited our discussions to work done by the group at North American Aviation. It is shown that both stable and radioactive isotopes can be used to advantage. Deuterium-labelling is widely used by numerous other investigators. Notable contributions in the use of radioisotopes have been made by Holroyd and Klein (14, 15) and Perner and Schuler 16) in their developments of radical sampling techniques.

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