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Publication Date
1959-12-01

UCRL 9056

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BERKELEY, CALIFORNIA

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UCRL-9056

UNIVERSITY OF CALIFORNIA

Lawrence Radiation Laboratory
Berkeley, California

Contract No. W-7405-eng-48

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December 1959

RADIOLYSIS OF ORGANIC LIQUIDS CONTAINING DISSOLVED ICN[1]

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In an earlier communication[3] we described some preliminary observations related to the use of ICN as a scavenger of labile intermediates formed in the radiolysis of organic liquids. Of particular interest was the finding that I_2 is a major product of radiation-induced reactions between ICN and the lower alcohols. In the present note we consider the mechanism of I_2 production in the ICN-methanol system. Brief reference is given to comparative data obtained with other organic solvents.

EXPERIMENTAL

The ICN was prepared by addition of I_2 to an aqueous solution of ICN (in excess).[4] Final purification was accomplished by sublimation under nitrogen. The colorless crystalline product contained less than 10^{-3} mole-percent I_2. Labelled compounds were prepared by direct exchange of ICN with NaI^{131} or $NaC^{14}N$. Methanol (Baker analyzed reagent) was redistilled over 2,4-dinitrophenylhydrazine and chromotopic acid. Cyclohexane (Phillips pure grade) was redistilled and twice recrystallized. All other chemicals were reagent grade

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(1) The work reported in this paper was performed under the auspices of the Atomic Energy Commission.

(2) Department of Chemistry, University of Liverpool, England

(3) G. Hughes and W. M. Garrison, Abstracts, Am. Chem. Soc. Paper No. 90 (133rd meeting, San Francisco, California, April 1958, Division of Physical and Inorganic Chemistry).

(4) Organic Synthesis, Vol. 32, John Wiley and Sons, New York, 1952, p. 29.

and were used without further purification.

Irradiations were made with γ-rays from a 1500-curie cobalt source.[5] Dosages were calculated from calibrations made with the Fricke dosimeter [$G(Fe^{+3})=15.5$].[6,7] Energy absorption in the various solutions was assumed proportional to density.

Iodine was determined spectrophotometrically in an absorption cell that formed an integral part of the irradiation vessel. Measurements were made at the wave length of maximum absorption by I_2 in each solvent. This value ranged from 450 mμ in methanol to 520 mμ in cyclohexane. Formation of organic iodides in I^{131}CN-cyclohexane solutions was measured in terms of I^{131} retention by the solvent after extraction of excess I^{131}CN with aqueous sodium sulfite. In studies with $IC^{14}N$, sulfite treatment was followed by acid hydrolysis and ether extraction. Aliquots of the latter were evaporated to dryness and assayed for C^{14} activity. Control runs established that solutions prepared by addition of ICN to each of the solvents both pure and pre-irradiated were stable in the dark for at least 24 hours.

Figure 1 shows typical date on I_2 production in evacuated ICN-methanol solutions. The initial rate is essentially independent of ICN concentration and corresponds to $G(I_2)=3.4$. The data obtained with solutions initially 10^{-3} M show that ICN is converted almost quantitatively to I_2 before any appreciable decrease in the rate of I_2 production occurs. Formation of I_2 in the earliest stages of the irradiation we attribute to reduction of ICN by H and (or) CH_2OH, the principal radical products from methanol.[8-10]

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(5) We are indebted to the Bio-organic Chemistry Group of the Lawrence Radiation Laboratory for the irradiation facility.

(6) C. J. Hochanadel and J. A. Ghormley, J. Chem. Phys. 21, 880 (1953).

(7) R. M. Lazo, H. A. Dewhurst and M. Burton, J. Chem. Phys. 22, 1370 (1954).

$$H + ICN \longrightarrow HCN + I \qquad (1)$$

$$CH_2OH + ICN \longrightarrow HCN + I + CH_2O \qquad (2)$$

$$2\ I \longrightarrow I_2. \qquad (3)$$

As soon as first traces of I_2 appear, the competing processes

$$H + I_2 \longrightarrow HI + I \qquad (4)$$

$$CH_2OH + I_2 \longrightarrow HI + I + CH_2O \qquad (5)$$

can occur. However, no net change in the rate of production of I_2 is introduced by reactions 4,5 as long as excess ICN is present because HI reacts quantitatively and almost instantly with ICN in organic media.[11,12]

$$HI + ICN \longrightarrow I_2 + HCN. \qquad (6)$$

Substantiating evidence for reaction 5 as written has been obtained from separate studies in which excess ICN was added to pre-irradiated I_2-methanol solutions. It was found that the I_2 concentration is immediately restored to within 90 to 95 percent of the initial value.[13] This observation is consistent with our proposal that the principal radical products from methanol viz H and CH_2OH, both react with I_2 to form HI.

On the basis of the mechanism given by reaction 1 through 6 inclusive, the total radical yield from methanol as measured by I_2 production in ICN-methanol

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(8) W. R. McDonell and A. S. Newton, J. Am. Chem. Soc., 76, 4651 (1954).

(9) G. E. Adams and J. H. Baxendale, J. Am. Chem. Soc., 80, 4215 (1958).

(10) N. N. Lichtin, J. Phys. Chem., 63, 1449 (1959).

(11) R. B. Mooney and H. G. Reid, J. Chem. Soc., 1318 (1933).

(12) Any removal of H via $H + CH_3OH \longrightarrow H_2 + CH_2OH$ does not affect the kinetics of I_2 production in this system, since no change in the total number of (reducing) radicals is involved.

(13) The fact that the observed recovery of I_2 is not quantitative in these experiments may be explained in terms of the reaction $CH_3 + I_2 \longrightarrow CH_3I + I$. Methyl radicals apparently account for some 5 to 15 percent of the total radical yield from methanol (ref. 8-10).

solutions is given by 2 $G(I_2)$=6.8. This measurement is in fairly good agreement with the values 6.1[9] and 6.3[14] recently obtained for methanol by use of ferric ion scavengers.

The radiation chemistry of ICN-hydrocarbon systems is considerably different than that of the alcohols. No net production of I_2 is found on radiolysis of cyclohexane and *n*-hexane containing ICN. However, we have established through the use of $I^{131}CN$ that alkyl iodides are formed as major products in both cases. Typical data on alkyl iodide production in evacuated ICN-cyclohexane solutions are shown in Fig. 2. The value G(RI) increases rapidly with ICN concentration over the range 10^{-4} *M* to 10^{-3} *M* but does not appear to approach a limiting value at ICN concentration as high as 10^{-2} *M*. At 10^{-3} *M* ICN, G(RI) $\simeq$ 2.2. From corresponding studies with $IC^{14}N$ we estimate that the yield of nitriles G(RCN) is less than 0.1. Since bond-energy date[15] indicate reactions of the type $R + ICN \longrightarrow RI + CN$ are endothermic by about 15 k cal., we venture the opinion that organic halides are formed predominantly by reaction of alkyl radicals with I_2 that is produced through H-atom reduction of ICN via reaction 1 above. Since alkyl radicals are produced in excess of H, no net production of I_2 from ICN is observed; direct experimental evidence for formation of H atoms in cyclohexane with a G-yield of ~2.1 has recently been reported.[16,17] It is likely that the increase in G(RI) observed with increasing

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(14) E. A. Cherniak, E. Collinson, F. S. Dainton and G. M. Meaburn, Proc. Chem. Soc., 54 (1958).

(15) T. L. Cottrell, The Strengths of Chemical Bonds, Butterworths Scientific Publications, London 1954, p. 178.

(16) G. Meshitsuka and M. Burton, Radiation Research 9, 152 (1958).

(17) We have found that addition of ICN to γ-irradiated solutions of I_2 in cyclohexane liberates I_2 ($HI + ICN \longrightarrow I_2 + HCN$) in amounts corresponding to G(HI) $\simeq$ 2.

ICN concentration above 10^{-3} M is related to processes of charge and (or) energy transfer. Some preliminary data recently obtained with ICN-benezene solutions appear to be interpretable only if such processes are invoked. These effects will be considered in a subsequent report.