

SHORT
COMMUNICATIONS

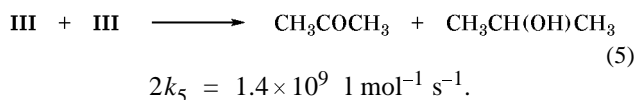
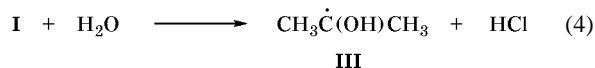
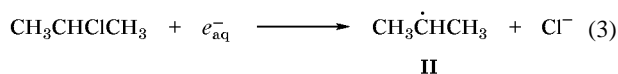
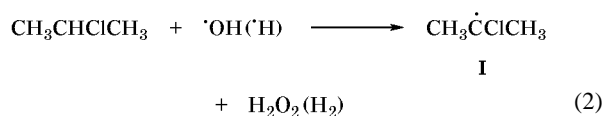
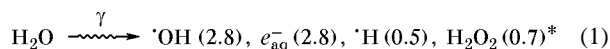
Nucleophilic Substitution in Radicals Derived from Isopropyl Chloride

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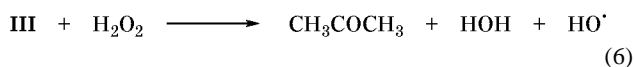
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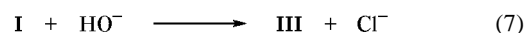
We previously studied nucleophilic substitution in terminal radicals derived from dichloromethane [1, 2], dichloroethane [3], and trichloroacetic acid [4]. The present communication reports on nucleophilic substitution in secondary radicals formed from isopropyl chloride. Radical species were generated by γ -irradiation of aqueous deaerated solutions of isopropyl chloride with a concentration of 0.04 M, containing different amounts of alkali. Chloride ions, acetone, and 2-propanol were detected as products. The formation of oxygen-containing products and increase in their yield with rise in the alkali concentration suggest that the process involves nucleophilic substitution of chlorine by hydroxide ion in radicals derived from isopropyl chloride. The obtained results are explained by the occurrence of reactions (1)–(16).



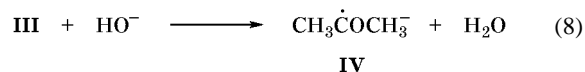
The fact that the yield of acetone is greater than the yield of 2-propanol is explained by reaction (6):



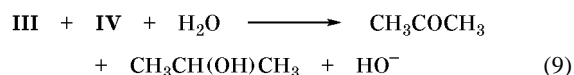
On addition of alkali, the substitution of chlorine in radicals **I** is accelerated due to reaction (7):



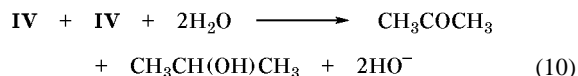
As a result, the rate of formation of radicals **III** increases, and the yields of acetone, 2-propanol, and Cl^- ions rise. In the presence of alkali radicals **III** are converted into radical anions **IV** via reaction (8):



The pK value of radical **III** is 12.2 [5]. At a NaOH concentration of 0.05 M (pH 12.7), the ratio of **III** and **IV** is almost equimolar. Acetone and isopropyl alcohol can be formed by reaction (9):

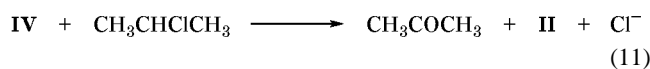


Further raising of the alkali concentration leads to increased conversion of radicals **III** into radical anions **IV**, and the rate of reactions (5) and (9) decreases. The reaction between similarly charged species **IV** [reaction (10)] is slower than the reaction with **III**:

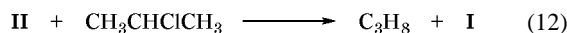


* In parentheses are given the radiation-chemical yields [6], molecule/100 eV.

The value $2k_{10}$ is equal to $4 \times 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ [5], i.e., it is lesser than $2k_5$ by a factor of 3.5. Therefore, the yield of 2-propanol decreases at an alkali concentration of 0.1 M and greater. Acetone is formed mainly by concurrent reaction (11), and the yield of acetone considerably exceeds the yield of 2-propanol.

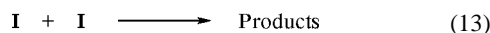


Reaction (11) is responsible for increase in the yield of chloride ions as the alkali concentration rises. The radiation-chemical yield of Cl^- ions is approximately twice as high as the overall yield of active species formed by radiolysis of water. This suggests chain character of the process leading to formation of chloride ions, which includes reactions (2), (7), (8), (11), and (12).



Ionizing radiation gives rise to establishment of a stationary concentration of radicals in solution, which depends on the radiation dose. Using the stationary concentration technique, the rate constants for nucleophilic substitution reactions (4) and (7) can be estimated. The stationarity condition implies that the rates of formation (v_f) and disappearance (v_d) of radicals be equal. In the case of radiation generation, $v_f = G_R I/N \times 100$, where G_R is the overall radiation-chemical yield of radical species formed by radiolysis of water (it is equal to 6.1 molecules/100 eV); I is the power of the absorbed radiation dose, equal to $2.1 \times 10^{18} \text{ eV l}^{-1} \text{ s}^{-1}$; and N is the Avogadro constant.

The rate of decay of radicals **I** is determined at least by their recombination (13), $v_d = 2k_{13} [\text{I}]_{\text{st}}^2$.



Then, $G_R I/N \times 100 \geq 2k_{13} [\text{I}]_{\text{st}}^2$, and the stationary concentration of radicals **I** can be calculated by the following equation:

$$[\text{I}]_{\text{st}} \leq \sqrt{G_R I/(N \times 100 \times 2k_{13})} \leq 1.2 \times 10^{-8} \text{ M}. \quad (14)$$

There are no data on k_{13} ; however, as a rough approximation, $2k_{13} = 2k_5$ may be assumed. Most probably, the rate-determining stage in the formation of acetone and isopropyl alcohol in neutral medium

is reaction (4). In this case, the rate of formation of acetone and isopropyl alcohol is equal to the rate of reaction (4), and

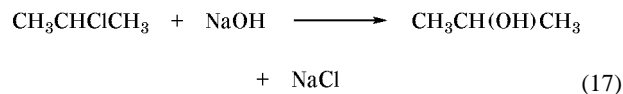
$$k_4 [\text{I}]_{\text{st}} [\text{H}_2\text{O}] = (G_a + G_i)I/N \times 100, \quad (15)$$

where G_a and G_i are the radiation-chemical yields of acetone and 2-propanol, which are equal, respectively, to 1.7 and 0.6 molecule/100 eV. Hence $k_4 \geq 0.12 \text{ l mol}^{-1} \text{ s}^{-1}$. In alkaline medium, at a low concentration of NaOH (0.05 M), the formation of acetone and isopropyl alcohol will be limited by reaction (7), and

$$k_7 [\text{I}]_{\text{st}} [\text{NaOH}] = (G_a + G_i)I/N \times 100. \quad (16)$$

From equation (16), k_7 is estimated at greater than or equal to $249 \text{ l mol}^{-1} \text{ s}^{-1}$. According to the calculations, the nucleophilicity of hydroxide ions is by a factor of ~ 2000 higher than the nucleophilicity of water molecules.

The formation of 2-propanol was also observed in alkaline solution without irradiation [reaction (17)], but the efficiency of this process was much lower.



The rate constant of reaction (17) (k_{17}), calculated from the time dependence of 2-propanol concentration, was $3.9 \times 10^{-7} \text{ l mol}^{-1} \text{ s}^{-1}$. The ratio k_7/k_{17} indicates that the efficiency of nucleophilic substitution in the radical derived from isopropyl chloride is greater by a factor of 6.4×10^8 than in the isopropyl chloride molecule.

Thus, secondary radicals formed from isopropyl chloride, as well as primary ClCH_2 radicals, are much more reactive (approximately by 9 orders of magnitude) in nucleophilic substitution than the parent molecules. Comparison of the obtained results with those reported in [1, 2] suggests the absence of steric inhibitory effect of methyl groups on nucleophilic substitution in radicals derived from 2-chloropropane.

The experimental conditions were similar to those described in [1]. Acetone and 2-propanol were determined by GLC using a 3-m column packed with 10% of PEG-400 on Chromosorb W (flame-ionization detector). The average errors in the determination of acetone, isopropyl alcohol, and chloride ions were 11, 9, and 12%, respectively.

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