Preparative-Scale Runs.—Isobutyl chloride (3.52 g) in 2 ml of carbon tetrachloride was irradiated with ultraviolet light and stirred while a solution of 2.2 g of chlorine in 20 ml of carbon tetrachloride was added during 2 hr. The reaction mixture was washed with aqueous 5% sodium bicarbonate and with distilled water and dried over Drierite. The solvent was removed by fractional distillation and the residual mixture of di- and trichloro derivatives was subjected to preparative gas chromatography in order to isolate the dichloro isomers, which were purified by a second gas chromatographic fractionation.

Registry No.—Isobutane, 75-28-5; isobutyl chloride, 513-36-0; *t*-butyl chloride, 507-20-0; 1,1-dichloro-2-methylpropane, 598-76-5; 1,2-dichloro-2-methylpropane, 594-37-6; 1,3-dichloro-2-methylpropane, 616-19-3.

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The Carbon-14 Isotope Effect in the Decomposition of *p*-Nitrophenethyl-1-^{14}C-trimethylammonium Iodide[1]

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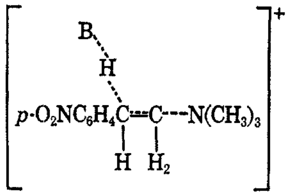
The decomposition of 2-(*p*-nitrophenyl)ethyl-2-*t*-trimethylammonium iodide to *p*-nitrostyrene and trimethylammonium iodide shows a tritium isotope effect, indicating that a hydrogen atom on the carbon atom which is adjacent to the ring is removed in the rate-determining step of the reaction.[2] When the decomposition occurs at 98° in an aqueous solution buffered to pH 6.0, the magnitude of the intermolecular isotope effect[3] is 2.12; the tritium-labeled molecule decomposes more slowly than the normal molecule. A study of the nitrogen isotope effect in this decomposition showed[3] that p-$O_2NC_6H_4CH_2CH_2{}^{14}N(CH_3)_3I$ decomposes under similar conditions approximately 2.4% faster than p-$O_2NC_6H_4CH_2CH_2{}^{15}N(CH_3)_3I$. The carbon–nitrogen bond is also broken in the rate-determining step of the reaction. A concerted mechanism was proposed for which the transition state could be represented as



$$\left[\begin{array}{c} \text{B}\cdots\text{H}\cdots \\ p\text{-}O_2NC_6H_4\underset{|}{\overset{}{C}}\text{=\!=}\underset{|}{C}\text{---}N(CH_3)_3 \\ \text{H}\quad\text{H}_2 \end{array}\right]^+$$

The proposed concerted mechanism would be further substantiated by the demonstration of an isotope effect in the decomposition of *p*-nitrophenethyl-1-^{14}C-trimethylammonium iodide, since in this case the bond to the carbon-14 atom would be broken in the rate-determining step of the reaction. Accordingly this specifically labeled compound was prepared[4] and the carbon-14 isotope effect in its decomposition was measured. The isotope effect, k^*/k, could be calculated from eq 1, which was developed by Downes and Harris.[5]

$$\frac{k^*}{k} = 1 + \frac{\log (N/N_0)}{\log (1 - f)} \tag{1}$$

Here N is the radioactivity of the recovered reactant after extent of reaction f and N_0 is the initial radioactivity of the reactant. Three runs were made by the procedure given and each product was assayed at least four times. The data from each run and the isotope effect calculated from that run are given in Table I.

TABLE I

DECOMPOSITION OF *p*-NITROPHENETHYL-1-^{14}C-TRIMETHYLAMMONIUM IODIDE

Run	Initial radioactivity of salt, μcuries/mmole	Radioactivity of recovered salt, μcuries/mmole	Extent of reaction, f	Isotope effect, k^*/k
1	2.84	3.04	0.613	0.928
2	3.02	3.27	0.690	0.932
3	3.00	3.28	0.697	0.925

Since the carbon-14 isotope effect in this reaction has an average value of 0.928 it seems certain that the decomposition of *p*-nitrophenethyl-1-^{14}C-trimethylammonium iodide is slower than that of the unlabeled compound. This is strong evidence that the carbon–nitrogen bond, which is shown here stretched, is broken in the rate-determining step, p-$O_2NC_6H_4CH_2CH_2 \ldots N^+(CH_3)_3$. Since a hydrogen atom on the carbon adjacent to the ring is also removed in the rate-determining step of the reaction, the proposed concerted mechanism for the reaction is further substantiated.

Experimental Section

The decomposition was performed by dissolving approximately 1.2 g of the iodide salt in 25 ml of solution buffered[6] to pH 7. Two 5-ml samples were withdrawn from the reaction mixture and the starting material was precipitated as the picrate, purified, and assayed to obtain the initial radioactivity of the salt. Three 5-ml samples of the reaction mixture were sealed in tubes and allowed to react for 5 hr in a bath at 100°, the reaction was stopped by precipitating the reactant as the picrate, and the latter was purified and assayed to give the radioactivity of the salt after a known extent of reaction. The weight of the picrate obtained from an aliquot of the reaction mixture by quantitative precipitation was used to calculate the extent of reaction. Three separate experiments were performed using this procedure.

Each sample was assayed four times by oxidizing to carbon dioxide with Van Slyke-Folch solution,[7] collecting the carbon dioxide in an ionization chamber, and measuring the ion current with a Model 30 Applied Physics Corp. vibrating reed electrometer. Since the readings on the vibrating reed electrometer were in the range of 150–250 mv and could be determined to ±0.2 mv, the relative radioactivities had uncertainties of 0.1–0.3%.

Registry No.—*p*-Nitrophenethyl-1-^{14}C-trimethylammonium iodide, 13391-71-4.

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