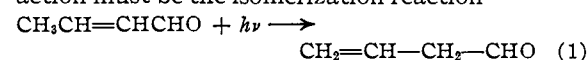


has produced new and novel results which we now report.

Gas chromatographic analysis using several columns of dinonyl phthalate on firebrick showed that after a short period of illumination a peak appeared which was later identified as 3-butene-1-al; somewhat later (*i.e.*, after 3-4 minutes) there appeared chromatographic peaks due to propylene, CO and 1,5-hexadiene. Some polymer also was formed but was not identified.

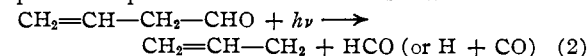
The identity of the 3-butene-1-al was established by preparing this compound by the oxidation of 3-butene-1-ol with CrO₃ in H₂SO₄ at 2-10°. This procedure was more successful than an attempted Oppenauer oxidation at 130°. Chromatographic analysis of the products of the Oppenauer reaction indicated that crotonaldehyde was the main product. The products from the CrO₃/H₂SO₄ oxidation of 3-butene-1-ol, however, on chromatographic analysis gave a peak at the same place as that found for the "new" product from the photolysis of crotonaldehyde. The infrared spectra of the product thought to be 3-butene-1-al from the photolysis and the compound resulting from the CrO₃/H₂SO₄ oxidation of 3-butene-1-ol were identical. That the oxidation product from 3-butene-1-ol was in fact 3-butene-1-al was confirmed by preparing the 2,4-dinitrophenylhydrazone. After recrystallizing the hydrazone twice from ethanol its m.p. (uncorrected) was found to be 175°, the literature value⁵ being 177°.

This observation that 3-butene-1-al is a product of the photolysis of crotonaldehyde shows that an important primary process in this photolytic reaction must be the isomerization reaction

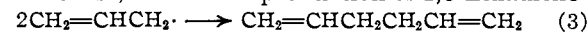


The quantum yield for this process is approximately 0.1 and is independent of the concentration of the crotonaldehyde and the light intensity over the range of variation studied. The production of 1,5-hexadiene which we also found is understood easily and its detection provides confirmatory evidence too that the photoisomerization (1) must occur.

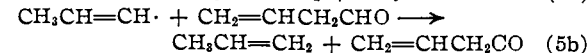
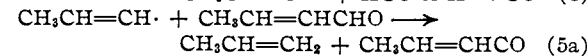
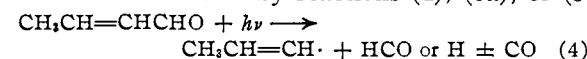
The photolysis of 3-butene-1-al would be expected to proceed in the manner shown



and the dimerization of the allyl radical would, of course, lead to the production of 1,5-hexadiene

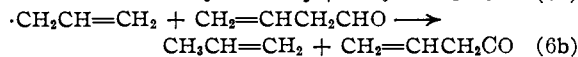
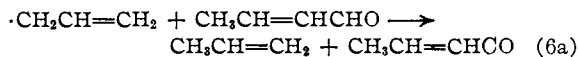


Propylene could be produced from the propenyl radical as indicated by reactions (4), (5a), or (5b)

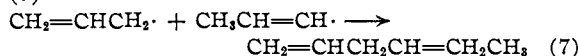


or more likely from the hydrogen abstraction reactions involving the allyl radical as shown in equations (6a) and (6b)

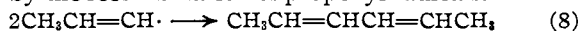
(5) M. F. Shostakovskii, A. V. Bogdanova and G. K. Krasilnikova, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk.*, 320 (1959); see *Chem. Abs.*, 53, 19941 (1959).



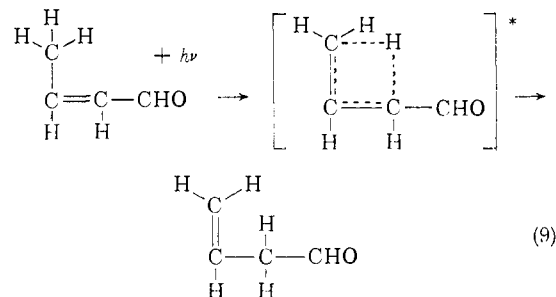
One would expect 1,4-hexadiene to be produced in the photolysis by the recombination reaction (7)



but so far we have not detected this compound. Nor have we been able to detect the presence of 2,4-hexadiene which conceivably could be formed by the recombination of propenyl radicals.



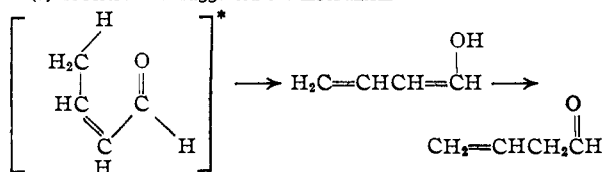
The mechanism of the photoisomerization of crotonaldehyde to 3-butene-1-al is suggested to be⁷



Acknowledgment.—We wish to thank the National Research Council of Canada for generous grants in support of this work.

(6) Holder of a National Research Council Studentship.

(7) A referee has suggested the mechanism



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NUCLEOPHILIC REACTIVITY OF THE HYDROGEN PEROXIDE ANION: DISTINCTION BETWEEN S_N2 AND S_N1 CB MECHANISMS

Sir:

It already has been shown that the anion of hydrogen peroxide is more reactive than hydroxide ion by factors as large as 10⁴ for a number of typical bimolecular nucleophilic displacement (S_N2) reactions.^{1,2} These have involved several different substrate molecules but to date no example of a displacement on a simple tetrahedral carbon compound has been studied kinetically. It is known that the reaction



gives hydroperoxide product in a number of cases.²

We would like to report the rate of reaction (1) where RX is benzyl bromide. The corresponding

(1) For a review see J. O. Edwards and R. G. Pearson, *J. Am. Chem. Soc.*, 84, 16 (1962); the enhanced reactivity is an example of what has been called the Alpha Effect.

(2) A. G. Davies, "Organic Peroxides," Butterworths, London, 1961, pp. 1-11.

TABLE I
RATE CONSTANTS IN 50% BY VOLUME ACETONE-WATER AT 25°

	Benzyl bromide	Si(acac) ₃ ^{a,d}
k_{OH^-}	$1.6 \pm 0.1 \times 10^{-3}$ M ⁻¹ sec. ⁻¹	1.7×10^8 M ⁻¹ sec. ⁻¹
$k_{O_2H^-}$	$5.4 \pm 0.1 \times 10^{-2}$ M ⁻¹ sec. ⁻¹	8.0×10^4 M ⁻¹ sec. ⁻¹

^a From reference 3.

TABLE II
0.10 Ethylenechlorohydrin 0.10 M base

H ₂ O ₂ , M	R ₁ /R ₂ obs.	R ₁ /R ₂ calcd.
0.088	5.6	5.5
0.096	4.0	4.0
2.0	.. ^a	..
None	.. ^b	..
0.0029 M Co(NH ₃) ₆ Cl ²⁺ , 0.0029 M base		
0.018	3.6	3.7
0.013	2.3	2.8
2.0	.. ^c	..
None	.. ^d	..

^a 2.4% base consumed in 10 minutes. ^b 37.5% base consumed in 10 minutes. ^c 2.5% chloride released in 10 minutes. ^d 62.5% chloride released in 10 minutes; data in water at 25°.

rate for hydroxide ion has also been measured. The solvent used was 50% by volume acetone-water and the analysis was by titration of released bromide ion. Good second order kinetics at 25° were observed for both reactions. The rate constants are given in Table I and it is seen that the O₂H⁻ ion is 35 times as reactive as the OH⁻ ion. Also shown are the two second order rate constants³ for the bimolecular displacement reactions of the two anions on tris-(acetylacetonato)-silicon(IV) complex, Si(acac)₃⁺, where it is observed that the O₂H⁻ ion is 50 times more reactive.

Results of this kind are more remarkable when it is recalled that hydrogen peroxide is nearly 10⁴ times as acidic as water. Thus the equilibrium constant for the reaction



is 150 in conventional units. The existence of equilibrium (2) and the results quoted in ref. 1 and Table I allow an easy distinction to be made between an SN₂ mechanism for a substrate which depends strongly on basicity in the nucleophile, and an SN₁CB (dissociation of conjugate base) mechanism. In the former case the addition of excess hydrogen peroxide to a reacting mixture of substrate and hydroxide ion will lead to an *increased* rate of reaction by a factor which may be as large as 10⁴. In the latter case there will be a *reduction* in rate by a factor as large as 150 for one molar H₂O₂. This is because an SN₁CB reaction has a rate directly proportional to the hydroxide ion concentration and reaction (2) greatly reduces this concentration. Equation (3) gives the ratio of rates of release of halide ion, or reduction of concentration of alkali, for runs with (R₂), and without (R₁), added H₂O₂.

$$R_1/R_2 = 1 + 150[H_2O_2] \quad (3)$$

Table II shows experimental values of R₁/R₂ compared to values calculated from (3) for several

(3) R. G. Pearson, D. N. Edgington and F. Basolo, *J. Am. Chem. Soc.*, **84**, 3233 (1962).

kinetic runs of the base hydrolysis of ethylene chlorohydrin and the chloropentammine cobalt(III) ion. These hydrolyses are generally believed to involve an SN₁CB mechanism.⁴ Values of R₁ found were in agreement with literature values. It is seen that hydrogen peroxide always inhibits the rate of halide release as predicted. Large amounts of hydrogen peroxide virtually stop the reaction as equation (3) predicts. Rapid decomposition of the peroxide occurs in these alkaline solutions,⁵ especially in the presence of cobalt ion, some of which is reduced to cobalt (II). Nevertheless, the release of halide ion is small as Table II shows. The results with the chloropentammine cobalt(III) are of special interest because of recent claims that the base hydrolysis of this and similar complexes goes by an SN₂ mechanism.⁶

Acknowledgment.—This work was supported by the U.S. Atomic Energy Commission under Contract No. AT-(11-1)-1087.

(4) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," Second Edition, John Wiley and Sons, Inc., New York, N. Y., 1961, pp. 288-305; R. G. Pearson, H. H. Schmitz and F. Basolo, *J. Am. Chem. Soc.*, **82**, 4434 (1960).

(5) The rate of decomposition of H₂O₂ in alkali is given by Rate = $k[H_2O_2][O_2H^-]$; F. R. Duke and T. W. Haas, *J. Phys. Chem.*, **65**, 304 (1961).

(6) C. K. Ingold, R. S. Nyholm and M. L. Tobe, *Nature*, **194**, 344 (1962).

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RECEIVED SEPTEMBER 27, 1962

FLUORIDE COMPLEXES OF PENTAVALENT URANIUM¹

Sir:

We wish to report a new and direct synthesis yielding fluoride complexes of U(V) in high purity. The technique involves direct combination of UF₆ with ammonium fluoride at 80-85° or with alkali fluorides in a sealed bomb at 350-400°. The identity of these compounds with those crystallized from concentrated aqueous HF establishes that these latter compounds contain U(V) in the non-oxygenated state.

Alkali fluoride complexes of uranium such as UF₄.*n*MF and UF₆.*n*MF are well characterized. (Note: Although undoubtedly complex fluorides, we write them as addition compounds solely for ease in showing the uranium oxidation state.) Few comparable compounds of pentavalent uranium are known.

The compound UF₆.3NaF was made² by limited fluorination of UF₄.3NaF. In a significant investigation published in report form, Rampy³ found that UF₆ was reduced by NH₃ below 33° to form white UF₅.NH₄F. However, Galkin, *et al.*,⁴ report that mixtures of UF₅ and UF₄.NH₄F result from NH₃ reduction at 25°. It seemed de-

(1) This work was sponsored by the U. S. Atomic Energy Commission.

(2) W. Ruedorff and H. Leutner, *Ann. Chem.*, **682**, 1 (1960).

(3) G. A. Rampy, GAT-T-697, 11-2-59, Goodyear Atomic Corp., available from U. S. Dept. of Commerce, Office of Tech. Services, Washington 25, D. C.

(4) N. P. Galkin, B. N. Sudarikov and V. A. Zaitsev, *Atomnaya Energiya*, **8**, 530 (1960), Consultant's Bureau Translation, **8**, 444 (1961).