directed toward the hydrogen atom that is also "up" according to Hund's rule for spin correlation in orthogonal atomic orbitals of atoms. The spin on the proton tends to be antiparallel to the spin of the carbon atom because of ordinary covalent exchange bonding, and thus the spin polarization on the hydrogen atom is opposite (or negative) to the principal spin polarization in the p_x carbon atomic orbital.

Spectroscopic Splitting Factors.—The measurements of the spectroscopic splitting factors are described in the Experimental section. The results are $g_x = 2.0026$, $g_y = 2.0035$ and $g_z = 2.0033$. The absolute value of any one g-factor is uncertain to ± 0.004 while the relative values are accurate to within ± 0.0001. In previous work[31] on the theory of g-factors for π-electron radicals, it has been pointed out that the deviation of the g-factors from the free electron value arises from spin–orbit interaction on the carbon atom combined with the virtual excitation of a σ-bonding electron to the π-orbital, and the virtual excitation of a π-electron to a σ^*-antibonding orbital. In the coördinate system of the present paper, this previous work indicated that the $\sigma \rightarrow \pi$ excitations increase g_y and g_z by $2\,\zeta/\Delta E_2$, and the $\pi \rightarrow \sigma^*$ excitations decrease g_y and g_z by $2\,\zeta/\Delta E_1$. Here $\zeta(= 28\ \text{cm.}^{-1})$ is the spin–orbit interaction parameter of atomic carbon,[32] and ΔE_1 and ΔE_2 are the $\pi \rightarrow \sigma^*$ and $\sigma \rightarrow \pi$ one electron excitation energies, respectively. Excitations of the type $\sigma \rightarrow \sigma^*$ do not contribute appreciably to g_x-deviations since contributions from the six $\sigma \rightarrow \sigma^*$ excitations cancel if all three σ (sp^2 hybrid) bonds are equivalent. The large $\sigma \rightarrow \sigma^*$ excitation energy also diminishes this contribution. This previous work[31] suggested that the g_y and g_z values would be slightly *greater* than the free spin g-factor and that g_x would be close to the free spin g-value in π-electron radicals. The present experimental results are in accord with these ideas.

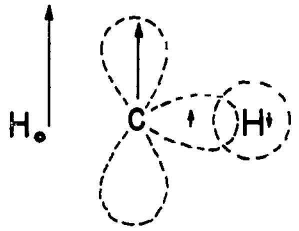

Fig. 12.—Spin polarizations on the α-carbon atom of $CH(COOH)_2$ and in the CH bond. The small spin density on the proton is negative (of opposite polarization) relative to the large π-electron spin density on the α-carbon atom.

Added in proof.—Zero-field resonance of $CH(COOH)_2$ has now been observed (H. M. McConnell, D. D. Thompson, and R. W. Fessenden, *Proc. Nat. Acad. Sci. U. S.*, **45**, 1600 (1959)). This work strongly supports the foregoing interpretation of the high field spectra.

Hyperfine splittings due to C^{13} in natural abundance in the central carbon atom have been observed (H. M. McConnell and R. W. Fessenden, *J. Chem. Phys.*, in press). This shows that the spin density in the hybrid orbital h_1 is positive, as illustrated in Fig. 12.

Pasadena, California

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(31) H. M. McConnell and R. E. Robertson, *J. Phys. Chem.*, **61**, 1018 (1957).

(32) D. S. McClure, *J. Chem. Phys.*, **20**, 682 (1952); **17**, 905 (1949).

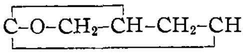
[Contribution from the Department of Chemistry, University of Rochester]

Photoisomerization of 5-Hexen-2-one[1]

By R. Srinivasan

Received August 24, 1959

The photochemistry of 5-hexen-2-one has been studied in the vapor phase in the temperature range from 27 to 139° at 3130 Å. and also with radiation from an unfiltered mercury arc. The compound was found to be very stable toward photolysis. The most important product at 3130 Å. up to 139° was an isomer, the structure of which is most probably CH_3–



$CH_3\text{–}C\text{–}O\text{–}CH_2\text{–}CH\text{–}CH_2\text{–}CH_2$

Evidence for this structure is based on the ultraviolet, infrared, nuclear magnetic resonance and mass spectra of the product. The quantum yield for the formation of the isomer was 0.006 at 3130 Å. The only other product at 3130 Å. that was identified was carbon monoxide. At shorter wave lengths, in addition to these products, methane, C_2 and C_3 hydrocarbons, acetone and biacetyl were identified. Although the ultraviolet absorption spectrum of 5-hexen-2-one resembles that of 2-hexanone, its photochemical stability is similar to that of unsaturated carbonyl compounds with the double bond conjugated with the carbonyl group.

Introduction

The photochemistry of unsaturated carbonyl compounds in which the double bond and the carbonyl group are conjugated, has been the subject of several investigations.[2–4] Two features appear to be peculiar to all these compounds as compared to the corresponding saturated carbonyl compounds. These are (i) the shift in the ultraviolet spectrum toward longer wave lengths and (ii) the stability of these molecules toward photochemical decomposition. As an illustration of the latter, it may be mentioned that the quantum yield for the production of carbon monoxide from crotonaldehyde is only about 0.05 at 250° and 3130 Å.[5] The present study of the photochemistry of 5-hexen-2-one in the vapor phase is believed to be the first one on an unsaturated carbonyl compound with an isolated double bond. In this instance, the ultraviolet spectrum was not expected to be

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(1) This research was supported in part by Contract AF18(600) 1528 with the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command. Reproduction in whole or in part is permitted for any purpose by the United States Government.

(2) W. A. Noyes, Jr., and P. A. Leighton, "The Photochemistry of Gases," Reinhold Publishing Co., New York, N. Y., 1941, p. 351.

(3) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Co., New York, N. Y., 1954, p. 317, 369.

(4) R. S. Tolberg and J. N. Pitts, Jr., This Journal, **80**, 1304 (1958).

(5) J. N. Pitts, Jr., D. D. Thompson and R. W. Woolfolk, quoted by J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

much different from that of the corresponding saturated compound, *i.e.*, 2-hexanone. Hence it was of interest to see the influence of the isolated double bond on the primary processes in this molecule.

Experimental

5-Hexen-2-one obtained from Eastman Kodak Company (white label) was fractionated at atmospheric pressure. A middle cut boiling over a range of 0.5° was collected. It was further purified by bulb to bulb distillation *in vacuo* and thoroughly degassed before use. By means of gas chromatography, the final sample was found to be essentially free from impurities.

Photolyses were carried out in a cylindrical quartz cell 20.0 cm. long and 3.9 cm. diameter. A conventional vacuum line in which the reactants did not come in contact with stop-cock grease was used. The light source was a Hanovia S-100 lamp filtered by 2 mm. of Corning 0-53 glass. The useful radiation was the group of lines at 3130 Å. The intensity of the radiation as calibrated by a diethyl ketone actinometer at 100° ($\Phi_{CO} \sim 1$) was 3.9×10^{15} quanta/sec. Photolyses were carried to 1% conversion.

The ultraviolet spectrum of 5-hexen-2-one as a solution in cyclohexane was recorded with a Cary spectrophotometer. The spectrum showed a maximum at 2815 Å. with a molar absorption coefficient of 22 and an inflection at about 2340 Å. This may be compared with the spectrum of 2-hexanone which has a maximum at 2790 Å. with an absorption coefficient of about 16.[6]

The products of the photolysis were identified by gas chromatography and mass spectrometry. Since the gaseous products were very little in all the experiments reported here, only the fraction volatile at −195° was measured quantitatively. It was essentially carbon monoxide. Quantitative measurements of the isomer of 5-hexen-2-one were made with a Perkin–Elmer Vapor Fractometer Model 154 and column "A." The instrument was calibrated by using 5-hexen-2-one as the standard, since it has been found that the thermal conductivity cell which is used as the detector has nearly the same sensitivity for isomeric substances.[7]

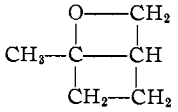
The isomer of 5-hexen-2-one was prepared in decigram quantity by photolyzing the ketone in the liquid phase. An AH-6 high pressure mercury arc was the source of radiation, and the Pyrex cell of 70 ml. capacity was concentric to the light source. Two water-cooled condensers attached to the cell and a stream of air from a blower maintained the temperature of the cell at about 80° in the irradiation zone. Considerable amounts of high-boiling products were observed to be formed during irradiation. After 22 hr., the photolysate was fractionally distilled. The first fraction (b.p. < 60°) was mostly acetone. The second fraction (b.p. ∼ 90°) was made up of the isomer contaminated with acetone, biacetyl and unreacted starting material. From this fraction, the pure isomer was separated by gas chromatography.

An attempt was made to collect the gas evolved during liquid phase photolysis and look for allene in this sample. It was concluded that allene, if formed at all, is only a minor part of the gaseous products.

Results

At 3130 A., 5-hexen-2-one was found to be very stable toward photodissociation to give gaseous products. Φ_{CO} was no more than 0.005 even at 139°.

At room temperature, the only product besides carbon monoxide that was formed in appreciable quantity was an unknown compound A. The highest peak in the mass spectrum of A, neglecting isotope peaks, was at an *m/e* value of 98. The compound was essentially transparent in the near ultraviolet, the molar absorption coefficient at 2100 Å. (solvent: 95% ethanol) being only 60. The infrared spectrum did not show the presence of carbonyl or hydroxyl groups or unsaturation. The strongest peak was at 950 cm.$^{-1}$ (trimethylene oxide)[8] and moderately strong peaks were observed at 934 and 1376 cm.$^{-1}$ ($-CH_3$). On the basis of this evidence, the structure of A may be



The nuclear magnetic resonance spectrum (Fig. 1) of the compound confirmed this structure since it showed (i) a single intense peak at 8.65 τ (3 protons) which was ascribed to the methyl group situated β to an oxygen atom, and with no proton on the carbon adjacent to it, (ii) two sets of peaks centered at 5.09 and 5.61 τ (each one proton) which can be attributed to the two protons on the carbon adjacent to the oxygen atom. Since these protons are non-equivalent and are also next to a carbon with one proton, the fact that each of these peaks is a quartet is explained satisfactorily,[9] (iii) a broad multiplet centered at 7.71 τ (4 protons) attributable to the protons in the two $-CH_2-$ groups which are part of a cyclobutane ring, (iv) a diffuse peak at 7.15 τ (one proton) which may arise from the single proton on the carbon β to the oxygen, (v) no evidence of unsaturation.

It was found impossible to identify the traces of other products that were formed during photolysis at 3130 Å. By use of an unfiltered mercury arc at high intensities, sufficient quantities of gaseous products were obtained to identify methane, ethylene, ethane, propane, propylene and a C_3 hydrocarbon which may have been allene. In the liquid products, acetone and biacetyl were detected.

Quantitative results for the production of carbon monoxide and the isomer of 5-hexen-2-one are given in Table I. It is observed that photoisomerization is the most important process at 3130 Å. over the temperature range studied, but even this proceeded with a quantum efficiency of only 0.006. The efficiency of isomerization appeared to be unaffected by a rise in temperature or the addition of oxygen. The ratio of isomer to carbon

TABLE I

PHOTOLYSIS OF 5-HEXEN-2-ONE VAPOR

Cell volume 238.6 ml. Corning 0–53 filter used except when stated otherwise.

Ketone press., mm.	Oxygen press., mm.	*I*a, quanta/sec. $\times 10^{-14}$	Time, min.	Temp., °C.	Rate of production Isomer molec./sec.	$CO \times 10^{-14}$
9.8		4.54	975	30.0	30	4.8
10.7		4.96	2767	27.1	30	3.2
11.9		4.45	910	102.8	26	14.9
10.4		3.59	907	139.0	24	19.5
9.0	12.6	4.23	975	26.9	25	N.d.[c]
11.0[a]		N.d.[c]	800	28.5	270	36.2
10.3[b]		N.d.[c]	120	28.5	900	1520
12.5[b]	16.5	N.d.[c]	120	30.0	800	N.d.[c]

[a] Corex filter. [b] Unfiltered arc. [c] N.d. not determined.

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(6) D. Biquard, *Bull. soc. chim. France*, **8**, 66 (1941).

(7) See also R. Srinivasan, This Journal, **81**, 5541 (1959), ref. 9.

(8) G. M. Barrow and S. Searles, *ibid.*, **75**, 1175 (1953).

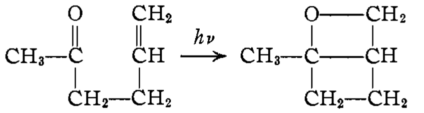
(9) These two peaks resemble those which arise from the two protons of the $-CH_2-$ in styrene oxide, presumably for similar reasons. See J. D. Roberts, "Nuclear Magnetic Resonance," McGraw–Hill Book Company, New York, N. Y., 1959, p. 48, 49.

monoxide was 8.0 at room temperature and decreased to 1.2 at 139° mainly because of an increase in the yield of carbon monoxide. A decrease in the wave length of the radiation also decreased the ratio, but it is not possible to say whether one or both processes were affected as the absorbed intensities were not measured under these conditions.

The quantum yield for the production of allene, if formed, was estimated to be less than 0.0005 at room temperature and 3130 Å. This estimate is based on the measurement of the fraction of product that was volatile at − 150° but not at − 195°.

Discussion

The formation of the isomer A from 5-hexen-2-one does not seem to involve any free radicals as intermediates as the process is unaffected by oxygen. Since the efficiency of the isomerization is independent of temperature, it is likely that the reaction proceeds intramolecularly, so that the process may be formulated as



(1)

The reaction is seen to be analogous[10] to the addition of carbonyl compounds to unsaturated hydrocarbons in solution under the influence of light.[11,12] Büchi and co-workers[12] have postulated a mechanism for this reaction which involves the triplet state of the carbonyl compound and proceeds in a stepwise fashion. It appears to be unnecessary to invoke this mechanism in the present instance. In fact, the absence of any effect on adding oxygen may be interpreted as evidence against the involvement of the triplet state of the molecule. The low quantum efficiency of the process may be due to the lack of sufficient substituents to stabilize the propylene oxide ring and also to the steric problem involved in forming a second 4-membered ring at the same time as the first one. Both these points may be clarified by studying this process in the photochemistry of unsaturated ketones in which the double bonds are four and five carbon atoms removed from the carbonyl group and with substituents at the double bonds.

The quantum yield for the production of carbon monoxide, which is a measure of the primary processes leading to free radicals (type I), is 0.005 at 139° and 3130 Å. This may be compared with the value of 0.139 for $\Phi_{CO+CH_4+C_2H_6}$ in 2-hexanone at 103° and 3130 Å.[13] and the value of 0.1 for Φ_{CO} in *trans*-methyl propenyl ketone at 275° and the same wave length.[4] It may be inferred from this that the presence of a double bond in a carbonyl compound confers a special stability to light and that this property is not dependent on the conjugation of the double bond with the carbonyl group.[14]

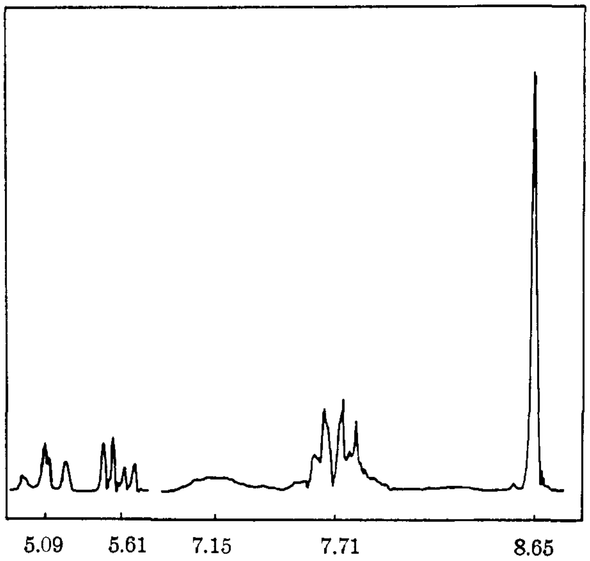


Fig. 1.—N.m.r. spectrum of product as a dilute solution in CCl_4; peak positions in τ units; Varian V-4311 spectrometer, 60 mc.; frequency standards $CHCl_3$ and $(CH_3)_4Si$.

The products identified in the present study suggest that both the primary processes

$$CH_3COCH_2CH_2CH{=}CH_2$$

$$\xrightarrow{h\nu} CH_3CO\cdot + \cdot CH_2CH_2CH{=}CH_2 \quad (2)$$

$$\longrightarrow CH_3\cdot + \cdot COCH_2CH_2CH{=}CH_2 \quad (3)$$

occur. Secondary reactions of free radicals would account for all the products if it is assumed that a free radical displacement reaction similar to the one proposed by Pitts and co-workers[15] in the photochemistry of crotonaldehyde and *trans*-methyl propenyl ketone is operative in this instance too.

Ketones with at least one hydrogen atom in the γ-position to the carbonyl group undergo a photochemical primary process (type II) involving the transfer of one hydrogen atom from the γ to the α position and a split in the bond between the α and β carbons. In 2-hexanone this process leads to acetone and propylene, the quantum yield being 0.45 at 3130 Å.[16] By analogy, this process may be expected to lead to acetone and allene in the case of 5-hexen-2-one. Although acetone was identified among the products, a corresponding amount of allene was not observed to be formed.[17] The acetone is probably mainly from the combination of methyl and acetyl radicals. The quantum yield of allene was no more than 0.0005 at 3130 Å. or $^1/_{10}$ of the quantum yield for the isomerization.

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[10] It is interesting to note that the reverse process, *i.e.*, the breakdown of the propylene oxide ring to give a carbonyl compound and an olefin also proceeds in the gas phase under the action of light. *Vide* J. D. Margerum, J. N. Pitts, Jr., J. G. Rutgers and S. Searles, THIS JOURNAL, **81**, 1549 (1959).

[11] E. Paterno and G. Chieffi, *Gazz. chim. ital.*, **39**, 341 (1909).

[12] G. Büchi, C. G. Inman and E. S. Lipinsky, THIS JOURNAL, **76**, 4327 (1954).

[13] W. Davis, Jr., and W. A. Noyes, Jr., *ibid.*, **69**, 2153 (1947).

[14] Ketene and its derivatives, which have a cumulative double bond, appear to be in a class by themselves with respect to their photochemistry.

[15] J. N. Pitts, Jr., D. D. Thompson and R. W. Woolfolk, THIS JOURNAL, **80**, 66 (1958).

[16] V. Brunet and W. A. Noyes, Jr., *Bull. soc. chim. France*, 121 (1958).

[17] It was suggested by one of the referees that allene may have been formed but that it may have gone undetected if it had polymerized almost immediately. We consider this to be unlikely in view of the fact that Guenther and Walters (THIS JOURNAL, **81**, 1310 (1959)) were able to detect allene as a product in the thermal decomposition of ketene even though the experimental conditions used by them were more drastic than ours.

It is to be concluded that the photochemical stability possessed by an unsaturated carbonyl compound extends to both type I and type II processes. The determination of the exact role of the double bond in the photochemistry of these compounds must await further experimental work.

Acknowledgments.—The author wishes to thank Professor W. Albert Noyes, Jr., for his continued interest in this work and Professors D. S. Tarbell and D. J. Wilson and Drs. R. M. Carman and D. D. Chapman for many helpful discussions.

ROCHESTER, NEW YORK

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Kinetics of the Oxidation of Halide Ions by Monosubstituted Peroxides

BY DONALD H. FORTNUM, CHARLES J. BATTAGLIA, STEPHEN R. COHEN AND JOHN O. EDWARDS

RECEIVED JUNE 25, 1959

The kinetics of some halide ion oxidations by peroxyacids have been investigated. The reaction of bromide ion with peroxymonosulfate has the rate law $R = k[Br^-][HSO_5^-]$ with a rate constant of 1.04 l. mole^{-1}-sec.$^{-1}$ at 25° and $\mu = 0.2$. The activation energy and entropy were found to be 10.6 kcal. mole^{-1} and -24.8 cal. mole^{-1}-deg.$^{-1}$, respectively. The oxidation of chloride ion by peroxymonosulfate has an analogous rate law and a rate constant of 1.4×10^{-3} l. mole^{-1}-sec.$^{-1}$. The activation energy and entropy were found to be 14.6 kcal. mole^{-1} and -24.1 cal. mole^{-1}-deg.$^{-1}$, respectively. The oxidation of bromide ion by peroxyacetic acid has the rate law $R = k[CH_3CO_3H][Br^-]$ with a rate constant of 0.258 l. mole^{-1}-sec.$^{-1}$ at 25° and $\mu = 0.2$; the activation energy and entropy are 13.7 kcal. mole^{-1} and -17.4 cal. mole^{-1}-deg.$^{-1}$, respectively. Peroxymonophosphoric acid oxidizes bromide ion with a rate which is first order each in peroxide concentration and in bromide ion concentration. The reaction was found to have an unusual *p*H dependence which has been interpreted in terms of the rate law $R = k_1[H_2PO_5^-][Br^-] + k_2[H_2PO_5^-][Br^-][H^+]$ and of the second ionization equilibrium constant K_2 of peroxymonophosphoric acid. Values of k_1, k_2, K_2 were found to be 3.2×10^{-2} l. mole^{-1}-sec.$^{-1}$, 9 l.^{2} moles^{-2}-sec.$^{-1}$ and 1.4×10^{-5}, respectively at $\mu = 1.5$ and 25°. Mechanistic conclusions are drawn.

Introduction

Caro's acid (peroxymonosulfuric acid) and the phosphorus analog have been long known, but until recently there have been few studies made of their chemistries, especially of the kinetics and mechanisms of reactions. Preliminary observations made in this Laboratory indicated that Caro's acid oxidizes halide ions to free halogens at markedly different rates. The reaction is "instantaneous" with iodide ion, rapid with bromide ion and slow with chloride ion.[1] The present study was undertaken to elucidate the kinetics and mechanism of the reaction of Caro's acid with halide ions and also to find out about the related reactions of peroxymonophosphoric acid and peroxyacetic acid with halide ions.

Experimental

Equipment. Bromide Oxidations.—Because the half-lives of these three oxidation reactions were less than a minute in the dilute solution ranges used here, the reaction was followed colorimetrically by measuring the absorption of bromine produced. A modified Bausch and Lomb "Spectronic 20" spectrophotometer equipped with a manual shutter and a special thermostated absorption cell was used. The absorption cell was a piece of 13 mm. outside diameter Pyrex glass tubing with a 25 mm. outside diameter Pyrex glass water jacket. Two brass endplates centered the inner tube in the jacket and provided an inlet and outlet for the filtered water, which was circulated to maintain constant temperature. The inner tube extended beyond the outer tube in both directions. The top was open to receive the sample and the bottom was connected to a short piece of Tygon tubing closed with a pinch clamp. The exposed portions of the jacket were painted black to eliminate stray light.

A 400-ml. beaker equipped with a Teflon plug stopcock at the bottom and surrounded by copper cooling coils to maintain constant temperature was used as the mixing vessel. The reactants were thoroughly mixed with a glass stirrer as the peroxyacid solution was added from a 1.5-ml. syringe held above the beaker by a holder constructed so that ejection of peroxide occurred simultaneously with starting of a stopwatch.

Caro's Acid-chloride.—This reaction was followed by determining the concentration of Caro's acid iodometrically in acid solution with standard sodium thiosulfate solution. A glass reaction vessel was assembled and immersed in a constant temperature bath. Nitrogen saturated with water vapor at the reaction temperature was continuously bubbled through the vessel in order to flush the liberated chlorine from the system.

Materials.—Laboratory distilled water and reagent grade chemicals were used except where otherwise specified. Caro's acid was prepared by treating BECCO 98% hydrogen peroxide with freshly distilled practical grade chlorosulfonic acid. With some modification in technique this is the method used by Ball.[2] The Caro's acid was diluted with cold water in a special ground glass stoppered mixing flask. When tested with silver nitrate the Caro's acid was found to be essentially free from chloride ion. Potassium dihydrogen phosphate-sulfuric acid buffers were used in the *p*H range 1 to 3 and potassium monohydrogen phosphate-potassium dihydrogen phosphate buffers at *p*H 5 to 6 for the Caro's acid oxidations.

The buffers employed in the peroxymonophosphoric acid reaction are listed in the table of rate data for this reaction. The peroxymonophosphoric acid solutions were made by acid hydrolysis of lithium peroxydiphosphate, $Li_4P_2O_8{\cdot}4H_2O$; the hydrolysis was stopped by dilution at the time calibrated for maximum yield of the monosubstituted peroxide. For the chloride oxidation, solutions of potassium chloride (2.00 *M*) and potassium nitrate (2.00 *M*) were prepared by diluting weighed samples of salt with the appropriate buffer solutions.

Peroxyacetic acid solutions were prepared by diluting BECCO 40% peroxyacetic acid with appropriate buffers. Solutions of sodium bromide (0.100 *M*) and sodium nitrate (0.100 *M*) were prepared in the same manner as before.

Procedure. Bromide Oxidations.—Preliminary studies were made to determine a procedure and concentrations of reactants that would give optimum results with the equipment. If the concentration of either reactant was too high the reaction proceeded too fast ($t_{1/2} < 15$ seconds). If the concentration of bromide ion was too low or if the concentration of peroxyacid was high, an appreciable fraction of the bromide ion was consumed. A very low concentra-

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[1] J. Girard and R. Carlson, unpublished experiments, Brown University.

[2] (a) D. L. Ball and J. O. Edwards, THIS JOURNAL, **78**, 1125 (1956); *J. Phys. Chem.*, **62**, 343 (1958); (b) D. H. Fortnum, Ph.D. Thesis, Brown University, 1958, p. 47.