character,[8] because such a transition state (essentially a zwitterion plus a bromide ion) should be considerably destabilized by transfer from water to a micellar pseudophase. On the other hand, if the transition state had considerable lactone character, one might expect the hydrophobic interactions between the micelle and the forming lactone plus those between the cationic micelle and the forming bromide ion to outweigh the energetically beneficial initial state interactions between the carboxylate ion and the cationic micelle so that the rate would not be retarded.

Catalysis of Decarboxylation of the 2-Cyano Acid II.—Although micellar catalysis is often interpreted in terms of a bringing together of reactants in a medium favorable for reaction, some unimolecular reactions are catalyzed by micelles.[3,9,11] Decarboxylations in which a carboxylate ion generates a carbanionlike transition state are strongly catalyzed by cationic micelles. The electrostatic interactions between the cationic micelle and the carboxylate ion assist the incorporation of the latter into the micelle and, of itself, this stabilization of the initial state would result in a rate reduction unless the transition state, with its delocalized negative charge, interacts more strongly with the micelle than the more localized carboxylate ion and offsets this rate reduction. As in the decarboxylation of 6-nitrobenzisoxazole-3-carboxylate ion (I),[3,12] we assume that added salts enhance the CTABr-catalyzed decarboxylation of 2-cyanophenylacetate (II) by reducing the charge density of the micelle. These positive salt effects upon micellar catalysis are unusual and have been observed only for decarboxylations.[12] In all other systems the counterions inhibit catalysis, presumably by excluding an anionic reactant from the micelle.[9–11] Added salts affect micellar structure;[12,19] for example they increase aggregation number, decrease the cmc, and cause the shape of the micelle to change from spherical toward rodlike, but, for all investigated reactions other than decarboxylations, it appears that these structural changes have no direct kinetic effects. For example, in the CTABr-catalyzed hydrolysis of the 2,4-dinitrophenyl phosphate dianion there is almost no increase of rate when the surfactant concentration is increased so much that the micelle becomes rodlike.[17] Decarboxylations appear to be more sensitive to micellar catalysis than most nucleophilic substitutions, where rate enhancements are often only *ca.* 10-fold, and are rarely more than 100-fold,[9,10] as compared with the 660-fold enhancement of the decarboxylation of II at 25°, and probably they are unusually sensitive to the charge density and nature of the micellar surface. When a cyanocarboxylate ion is incorporated into a cationic micelle the negatively charged carboxylate residue will probably be in the water-rich region, where it will suffer electrostatic repulsions if added anions build up in the Stern layer, and added salts should destabilize the initial state. On the other hand, this negative charge becomes delocalized into the carbanionlike transition state where it will be closer to the quaternary ammonium groups of the surfactant and therefore relatively unaffected by anions in the Stern layer.

Registry No.—II, 34220-42-3; IV, 25297-23-8; CTABr, 57-09-0; 3-phenylpropionate ion, 826-17-5.

[19] K. Shinoda, T. Nakagawa, B. I. Tamamushi, and T. Isemura, "Colloidal Surfactants," Academic Press, New York, N. Y., 1963; K. Shinoda, *J. Phys. Chem.*, **59**, 432 (1955); K. J. Mysels and L. H. Princen, *J. Colloid Sci.*, **12**, 594 (1957).

Autoxidation of Esters. I. Isobutyl Acetate

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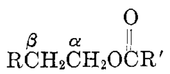
Isobutyl acetate was treated with oxygen in the temperature range 100–120°. This autoxidation reaction seems to proceed as the analogous one with isobutane, but the primary product is, apparently, much less stable. The 2-hydroperoxyisobutyl acetate decomposes to acetone, formaldehyde, and acetic acid at a rate comparable to its rate of formation. In some respects, this decomposition seems not to involve radical intermediates. The formaldehyde is readily oxidized further to formic acid. Carbon monoxide, hydrogen, isobutyric acid, and 2-oxopropyl acetate are minor products in the isobutyl acetate oxidation. The oxidation kinetics conform to the usual free-radical chain mechanism rate expression with little complication.

The reaction of hydrocarbons with oxygen is one of the most thoroughly studied[1] reactions of organic chemistry; yet, the amount of information available on oxygen-containing derivatives is surprisingly small. Aldehydes,[2] ethers,[3] and alcohols[4] are the most closely studied of the oxygen-containing compounds.

Although the oxidation of unsaturated fatty acid esters[5] has been intensively studied, information is lacking on simple esters where the ester function and the oxidatively labile hydrogen are in proximity. In particular, the autoxidative attack on the alcohol portion of an ester at the α and β positions is the major interest here.



$$\overset{\beta}{\mathrm{RCH_2}}\overset{\alpha}{\mathrm{CH_2}}\mathrm{O}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}\mathrm{R'}$$

1

From the few data available in the present literature it appears that trying to investigate oxidative attack

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[1] Relatively recent reviews of the subject include L. Reich and S. S. Stivala, "Autoxidation of Hydrocarbons and Polyolefins," Marcel Dekker, New York, N. Y., 1969; F. R. Mayo, *Accounts Chem. Res.*, **1**, 193 (1968); J. Betts, *Quart. Rev., Chem. Soc.*, **25**, 265 (1971).

[2] G. E. Zaikov, J. A. Howard, and K. U. Ingold, *Can. J. Chem.*, **47**, 3017 (1969).

[3] J. A. Howard and K. U. Ingold, *ibid.*, **47**, 3809 (1969); **48**, 873 (1970).

[4] C. F. Cullis and A. Fish in "The Chemistry of the Carbonyl Group," S. Patai, Ed., Interscience, New York, N. Y., 1966, Chapter II, pp 79–186.

[5] W. O. Lundberg, Ed., "Autoxidation and Antioxidants," Interscience, New York, N. Y., 1962. Several chapters deal with fatty acid autoxidation.

at the α position may be unrewarding. Although benzyl acetate[6] is moderately reactive in autoxidation to give an 80% yield of titratable hydroperoxide at 30° and gas-phase oxidation of ethyl acetate[7] at 250–400° has been postulated to occur at the α position, simple esters seem inert in the liquid phase. Buxbaum was unable to obtain any useful reaction between oxygen and ethylene dibenzoate[8] up to 200°, and isopropyl acetate[9] could not be oxidized at a reproducible rate or product yield in the temperature range 135–150°. The sensitivity of the oxidation to the purity of the ester was attributed to hydrolysis and the oxidative reactivity of isopropyl alcohol, which was much higher than the reactivity of the ester. *In situ* conversion of alcohols to borate esters[10] to protect them from further oxidative attack is a well-known technique.

Reported in this paper are the results of a detailed investigation of the liquid-phase autoxidation of isobutyl acetate, one of the simplest possible substrates where a reactive (tertiary) hydrogen is β to the ester function. This ester is a simple analog of the well-studied isobutane[11] where one methyl group has been replaced by an acetoxymethyl group. Some less complete data on the autoxidation of the bifunctional compound *trans*-1,4-cyclohexylenedimethylene diacetate are presented in another paper.[12]

Experimental Section

Materials.—Isobutyl acetate (IBAc), isobutyl benzoate (IBBz), and isopentyl acetate (IPAc) were Eastman reagent-grade materials and were distilled before use. The IBAc contained low levels (~0.5%) of either butyl acetate or ethyl isobutyrate, depending on the lot. Neither impurity at this level is expected to have an effect on the results. Methyl benzoate, used as a reaction solvent, was also an Eastman reagent-grade compound and was also distilled. Initiators were Lucidol 99% *tert*-butyl peroxide, which was used directly, or Columbia Organic 1,1′-azodicyclohexanecarbonitrile, which was recrystallized from methanol–acetone. All other materials were reagent-grade chemicals and were used directly.

2-Oxopropyl Acetate.—This material, anticipated as a possible product in the oxidation,[5] was synthesized by direct acetylation of 1-hydroxy-2-propanone (Eastman Organic Chemicals No. 10646). 1-Hydroxy-2-propanone (14.8 g, 0.2 mol) in 75 ml of pyridine was mixed with 20.4 g of acetic anhydride and allowed to stand overnight. Distillation of the mixture gave 8 g of product: bp 124–127° (150 mm) [lit.[13] bp 65° (11 mm)]; nmr ($CDCl_3$, 60 MHz) δ 2.08 (s, 6, CH_3, CH_2OOCCH_3), 4.58 (s, 2, $COCH_2OOCCH_3$). 2-Oxopropyl acetate was detected in small amounts (see Results and Discussion) in IBAc oxidations by comparison of mass spectral–glpc effluent patterns with those of the authentic material.

2-Hydroxy-2-methylpropyl Acetate (2).—This material seemed to be incompletely described in the literature; it was expected to be the major product (following reduction of the corresponding hydroperoxide) from the oxidation of IBAc. Sodium acetate (5 g) was dissolved in acetic acid (35 ml) by warming on a steam bath; then 5.0 ml of 1,2-epoxy-2-methylpropane (Columbia Organic) was added by syringe, and the mixture was kept on a steam bath for 1 hr. The reaction mixture was poured into water, sodium hydroxide solution was added until the mixture was neutral, and then the mixture was extracted with ether. Distillation of the ether extracts yielded 3.5 g of oil which, by nmr, was 85% desired product. Repetitive, preparative glpc (Carbowax 20M column) of the oil yielded 1.0 g of analytical sample used for making standard solutions for glpc calibration: nmr ($CDCl_3$, 60 MHz) δ 1.20 [s, 6, $(CH_3)_2C$], 2.05 (s, 3, $OOCCH_3$), ~3 [s, 1, $(CH_3)_2COH$], 3.88 (s, 2, CH_2OOCCH_3).

Oxidation Procedure.—Initiator and ester were made up in reaction bulbs of 54- or 104-ml capacity and shaken with oxygen at 100 or 120°. The apparatus used has been previously described, along with the procedure for calculating the rates.[14] At the conclusion of a run, in some cases, the gases in the reaction bulb void space were sampled for glpc analysis before final degassing of the bulb, detachment from the apparatus, and weighing.

Analysis Procedure.—Oxidates were titrated[15] first for hydroperoxide by the usual iodometric procedure and then for free carboxylic acid with 0.1 *N* sodium hydroxide. An approximately 25-g aliquot of the oxidate was reduced[16] with triphenylphosphine by the addition of 15% excess (as indicated by the iodometric titration) in a small amount (~2 ml) of IBAc. The reduced mixture was then distilled at ~10 mm with the pot temperature kept at 30° or less and the receiver maintained at −200°. An aliquot of the weighed distillate was made up with benzene as an internal standard and analyzed for undecomposed *tert*-butyl peroxide, acetone, and *tert*-butyl alcohol by glpc (Carbowax 20M column). The pot residue was quantitatively collected with benzene as the solvent, made up with mesitylene as an internal standard, and analyzed for **2** by glpc (Carbowax 20M). Both glpc analyses were calibrated with authentic samples. Also, sufficient pot residue from one oxidation run was collected from the glpc effluent to obtain an nmr spectrum and confirm the assigned structure of **2**. About one-sixth of the total amount of **2** was carried over into the distillate by this procedure, and the total yield of this product was corrected accordingly.

The acid products of this reaction could not be satisfactorily analyzed directly by glpc. To apportion the total yield of acid as determined by titration, the acidic fraction of an oxidation was isolated and converted to propyl esters for glpc analysis as follows. Following reduction of an oxidate sample, sufficient aqueous sodium hydroxide (0.1 *N*) was added to the mixture to convert all acids to sodium salts. The aqueous phase was isolated, washed with ether, acidified (pH 1), and continuously extracted with ether for 24 hr. The ethereal solution of acids was dried ($MgSO_4$) and concentrated to ~20 ml by distillation under reflux. The pot residue was then esterified with propanol–BF_3 reagent and worked up for glpc analysis as described.[17] Propyl formate, acetate, and isobutyrate were identified by com. parison of their retention times with those of authentic samples- The effectiveness of the procedure was checked by esterifying a known mixture of the three acids in a like manner.

Results and Discussion

Most of the rate and product data of this investigation are summarized in Table I. Supplementary data are contained in Tables II and III.

Rate Law for the Oxidation. Order in Substrate Concentration.—Figure 1 shows a plot of the initial rate of oxygen consumption (R_0) *vs.* the concentration of IBAc for 120° runs where the *tert*-butyl peroxide concentration was near 0.038 *M*. For the pure methyl benzoate solvent (run 13, Table I), the observed rate was increased by the factor $(0.038/0.0128)^{1/2}$ to correct for the lower initiator concentration. As indicated, methyl benzoate, chosen because of its similar polarity to IBAc, is not completely inert under the oxidation conditions so that a cooxidation of the two esters was actually performed. A good linear correlation was obtained and indicated first-order dependence on the

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(8) L. H. Buxbaum, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **8** (1), 552 (1967).

(9) T. Mill, Stanford Research Institute, private communication.

(10) W. G. Woods and R. J. Brotherton in "Progress in Boron Chemistry," Pergamon Press, Oxford, 1970, p 1.

(11) D. L. Allara, T. Mill, D. G. Hendry, and F. R. Mayo, *Advan. Chem. Ser.*, **76**, 40 (1968).

(12) D. E. Van Sickle, *J. Org. Chem.*, **37**, 1398 (1972).

(13) G. F. Hennion and W. S. Murray, *J. Amer. Chem. Soc.*, **69**, 1221 (1942).

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(15) R. D. Mair and A. J. Graupner, *Anal. Chem.*, **36**, 194 (1964). "Hercules Method I" was used.

(16) D. B. Denney, W. F. Goodyear, and B. Goldstein, *J. Amer. Chem. Soc.*, **82**, 1393 (1960).

(17) H. Salwim and J. F. Bond, *J. Ass. Offic. Anal. Chem.*, **52**, 41 (1969).

TABLE I

OXIDATION OF ESTERS[a]

Charge and rate data							Product yields				
Run	[*tert*-Bu_2O_2], M	IBAc, mmol	Volume, ml	Time, min	O_2 absorbed, mmole	$R_0 \times 10^4$,[b] M min^{-1}	Total $-O_2H$,[c] mmol	Total $-COOH$,[d] mmol	$(CH_3)_2C$-$(OH)CH_2$ OAc,[e] mmol	$(CH_3)_2CO$, mmol	*tert*-BuOH, mmol
						120°					
1	0	297.0	45.7	1775	5.6	0.38[f]	1.21	6.07	1.36	2.81	
2	0	301.0	46.3	1445	3.2	0.23	1.32		1.26	1.83	
3	0.0098	297.0	45.9	495	2.7	1.2	1.25	2.23	1.09	1.00	0.32
4	0.0200	298.0	46.0	1460	13.7	1.9	0.30	17.10	2.55	~10.20	1.12
5	0.0202	598.0	92.5	495	8.4	1.9	3.05	6.75			
6	0.0375	299.0	46.0	495	4.9	2.3	1.98	3.70			
7	0.0386	297.0	46.0	410	4.9	2.5	1.71	3.66	1.81	2.56	0.74
8	0.0391	597.0	92.6	410	9.6	2.7	3.41	7.71			
9	0.0400	300.0	46.2	1200	7.5	2.5	0.37	8.02			
10	0.0908	299.0	46.7	275	5.2	4.2	1.99	4.05			
11[g]	0.0375	148.0[g]	45.0[g]	505	2.9	1.5	1.15	2.30			
12[g]	0.0381	76.3[g]	45.2[g]	475	1.8	1.0	0.63				
13[g]	0.0128	0[g]	42.9[g]	400	~0.3	0.22	0.10				
14[h]	0.0167	299.0	56.2	170	8.3	~9.8	0.23				
15[i]	0.0213	299.0	48.4	360	4.6	1.3	1.83	3.15	1.07	0.90	0.58
16[j]	0.0394	299.0	47.5	410	5.8	2.9	2.38				
17[k]	0.0423	223.0[k]	44.1	495	3.6	2.4	1.82	3.04			
18[l]	0.0404	265.0[l]	46.5	85	4.0	11.5	1.93	1.35			
						100°					
19	0.0400	299	44.9	2110	2.5	0.30	1.24	1.97	1.34	0.75	0.43
20	0.0423	299	45.0	1830	2.7	0.38	1.12	2.26	1.14	1.14	0.47
21	0.0790	299	45.3	1510	3.1	0.45	1.23	2.48	1.32	1.15	0.65
22	0.0402[m]	299	44.6	225	5.9	9.2	2.00	3.42			
23[n]	0.0403	277	47.1	1525	7.0	1.4	−0.80[o]				

[a] Oxygen pressures ranged from 3 to 6 atm. [b] Initial oxygen uptake rate. [c] By iodometric titration. [d] By base titration. [e] After triphenylphosphine reduction. [f] Final (steady from t = 1300 min to end), rate = 0.88 M min^{-1}. [g] Methyl benzoate solvent. [h] 104.0 mmol of acetic anhydride present. [i] 21.7 mmol of isobutyl alcohol in initial charge. [j] 1.0 ml of water (58 mmol), added at start gives single phase at the 120° reaction temperature. [k] Isobutyl benzoate. [l] Isopentyl acetate. [m] 1,1′-Azodicyclohexanecarbonitrile initiator. [n] 47.5 mmol of *tert*-butyl hydroperoxide was added. [o] Net decrease in $-O_2H$ titer.

TABLE II

ACID CONTENT OF ISOBUTYL ACETATE OXIDATIONS AT 120°

								Acid yield, mol % of total		
Run	[*tert*-Bu_2O_2], M	IBAc, mmol	Time, min	O_2 consumed, mmol	Convn, %	Total $-O_2H$, mmol	Total $-COOH$, mmol	HCOOH	CH_3COOH	$(CH_3)_2CH$ COOH
24	0	600	1400	7.5	1.25	2.50	6.45	18.2	77.5	3.8
25	0.024	373	1125	13.8	3.70	1.37	16.41	20.5	75.3	4.2

TABLE III

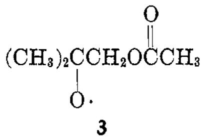
GAS YIELDS OF ISOBUTYL ACETATE OXIDATIONS AT 120°

			Gas yields, mmol	
Run	O_2 consumed, mmol	Convn, %	CO	H_2
4	13.7	4.60	3.80	1.89
3	2.7	0.91	0.34	0.10
7	4.9	1.65	0.82	0.06
8	9.6	1.61	1.30	0.20
24	7.4	1.23	0.72	0.13
17[a]	3.6	1.61	0.54	0.02
18[b]	4.0	1.51	0.09	0.01
25	13.8	3.70	4.21	0.89

[a] Isobutyl benzoate. [b] Isopentyl acetate.

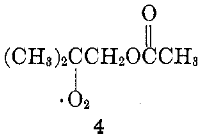
IBAc concentration; it further indicated that the oxidation is not sensitive to participation by solvent-derived radicals; *i.e.*, an ideal cooxidation[18] is obtained. Active tertiary hydrogen substrates, in particular cumene,[19] often show marked deviation from ideality.

These results also suggest that this system is significantly different from the analogous isobutane[11] oxidation where the *tert*-butylperoxy radical enters into a bimolecular, nonterminating reaction to produce *tert*-butoxy radicals. At high IBAc concentration, **3** would be converted to **2**.



$(CH_3)_2C(O\cdot)CH_2OC(=O)CH_3$

3



$(CH_3)_2C(\cdot O_2)CH_2OC(=O)CH_3$

4

The possibility of the conversion of the chain carrier radical **4** to **3** as a significant reaction in the mechanism is discussed in the section on products. A comparison of the absolute oxidation rates of the IBAc and isobutane systems infers that a much faster termination exists in the IBAc system than in the isobutane system. At 100° with *tert*-butyl peroxide (0.0619 M), neat isobutane (7.46 M) oxidizes[11] at a rate of 3.5×10^{-4} M min^{-1}. At the same temperature and comparable initiator concentration (run 21, Table I), neat IBAc (6.6 M) oxidizes at 0.45×10^{-4} M min^{-1}.

Order in Initiation Rate.—In Figure 2 the oxidation

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[18] F. R. Mayo, M. G. Syz, T. Mill, and J. K. Castleman, *Advan. Chem. Ser.*, **75**, 38 (1968).

[19] G. A. Russell, *J. Amer. Chem. Soc.*, **78**, 1047 (1956).

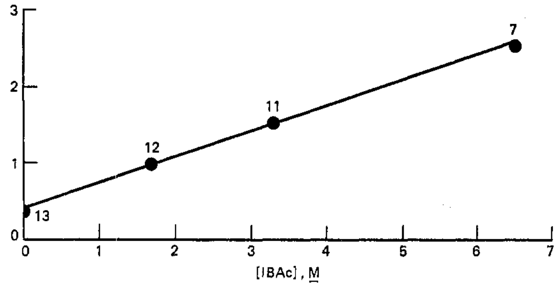


Figure 1.—Substrate concentration rate dependence.

rates of neat (6.5 *M*) IBAc at 120° are plotted against the initiator concentrations on a log–log scale. A straight line is obtained over a tenfold range of *tert*-butyl peroxide concentration, and the slope of the line is 0.52, probably identical within experimental error to the theoretical value of $^1/_2$ which applies for simple oxidations. Thus, some of the complications which lead to nonrational[20] initiation orders are absent in this reaction.

In particular, the thermal initiation rate is apparently minor compared to that from the added *tert*-butyl peroxide. The estimation of the initial thermal rate, 0.3×10^{-4} *M* min^{-1} (runs 1 and 2, Table I), suggests that, where *tert*-butyl peroxide is ~0.02 *M*, the ratio of initiation rates is $(1.9/0.3)^2 = 40/1$. Also, the onset of autocatalysis is relatively slow with the rate of the thermally initiated run slowly rising to $\sim 0.88 \times 10^{-4}$ *M* min^{-1}. Initiated oxidations of IBAc at 120° show either no autocatalysis or a slight diminution of rate, as shown by Figure 3. These results contrast with the oxidation of the cyclohexylenedimethylene diacetate, described in another paper.[12]

Temperature Effect.—Only two temperatures were investigated due to the low reactivity of IBAc. At 100° with *tert*-butyl peroxide (0.0400 *M*), the rate is 0.30×10^{-4} *M* min^{-1} (run 19, Table I) *vs.* the expected rate of 2.7×10^{-4} *M* min^{-1} (read from Figure 2) at 120°. A two-point Arrhenius plot of these data indicates an overall activation energy (E_a) of 32 kcal/mol. Assuming the rate law is of the form

$$R_0 = K[tert\text{-}Bu_2O_2]^{1/2}[IBAc] \qquad (1)$$

and the activation energy[21] for *tert*-butyl peroxide is 37 kcal/mol, the overall activation energy exclusive of the initiation step is

$$\Delta E = 32 - (^1/_2)(37) = 14 \text{ kcal/mol}$$

If, as argued in the preceding sections, the termination is the relatively low activation process of a primary (or secondary) and a tertiary peroxy radical combination (E_a ~3), then the net activation energy of the propagation reaction would be ~15 kcal/mol. This assumes that eq 1 in the complete form is

$$R_0 = (R_i/2k_t)^{1/2}k_p[IBAc] \qquad (2)$$

where k_p is the rate constant for propagation, k_t the rate constant for termination, and R_i the rate of initiation, related to the concentration of *tert*-butyl peroxide by

$$R_i = 2k_d[tert\text{-}Bu_2O_2] \qquad (3)$$

where k_d is the rate constant for the decomposition of *tert*-butyl peroxide. The 15-kcal activation energy associated with k_p is the same value calculated for the isobutane[11] oxidation.

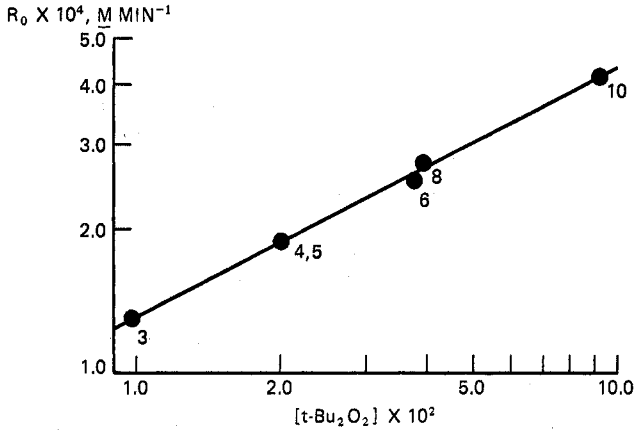


Figure 2.—Effect of initiator concentration.

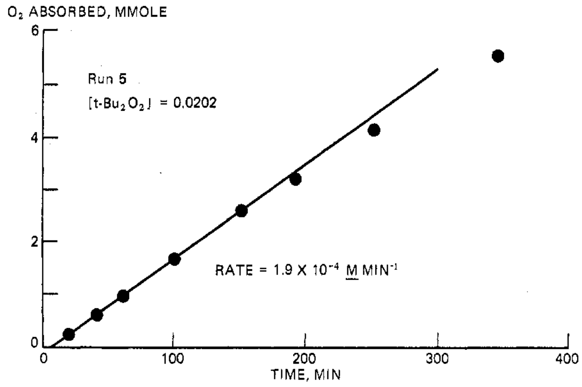
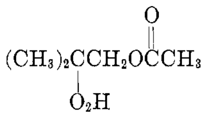


Figure 3.—Oxygen absorption of isobutyl acetate.

Products of Oxidation.—As can be seen from Table I, hydroperoxide yields are only ~40% of the oxygen absorbed. After triphenylphosphine reduction of the oxidate, the amount of **2** found corresponds quite closely to the hydroperoxide content. Therefore, it was assumed that, at most of the conversions studied, the hydroperoxide **5** accounted for ~40% of the oxygen consumed.



$$(CH_3)_2C(O_2H)CH_2OC(=O)CH_3$$

5

Only in the high conversion run 145 (Table I), where reaction was continued until oxygen in the bulb void space was exhausted, did **2** substantially exceed the hydroperoxide yield.

Aside from *tert*-butyl alcohol, which arises from initiator fragments, the only other product reliably detected in the glpc analysis was acetone. Peaks which were later identified as those of acetic and isobutyric acids were present but did not account quantitatively for the acid titrated. Calculation of the amount of *tert*-butyl alcohol which should be formed if all peroxide which decomposes is converted to this product agrees within 0.1 to 0.2 mol of alcohol actually found. Previously published[21] values for the decomposition rate of *tert*-butyl peroxide were used to calculate the number of *tert*-butoxy radicals formed. Therefore, all of the

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[20] D. E. Van Sickle, *J. Org. Chem.*, **37**, 755 (1972).

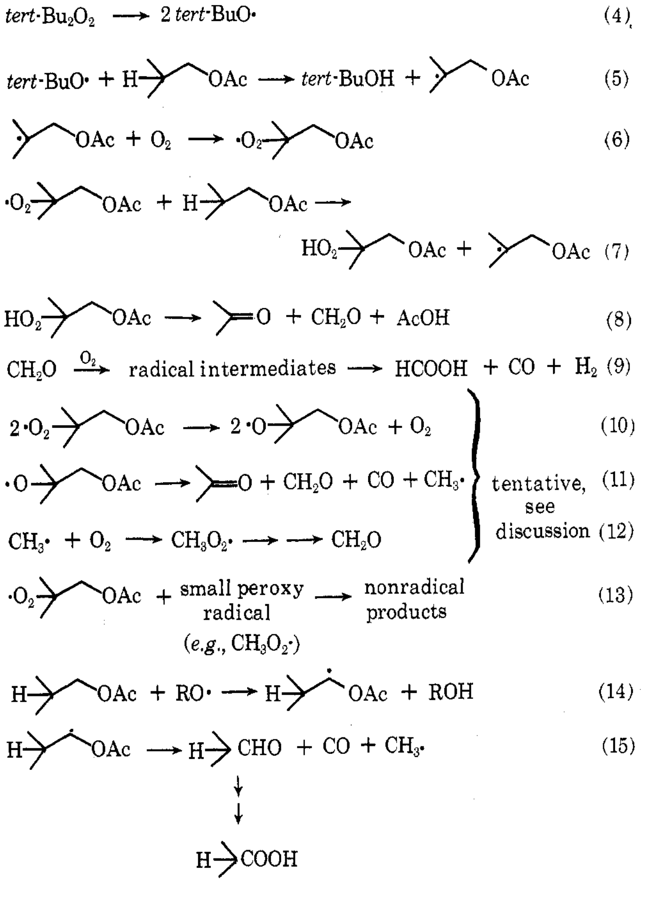
[21] P. Molyneux, *Tetrahedron*, **22**, 2929 (1966), and references cited therein. The "best" value of E_a for *tert*-butyl peroxide is 37.8 ± 1.0 kcal/mol.

acetone found in the IBAc oxidations was assigned to the substrate itself and not to fragmentation of the *tert*-butoxy initiator radicals.

As indicated previously, direct glpc analysis for the acids present in the product mixture was not effective. To determine the nature of the acids present, two oxidation runs were made which were worked up to isolate the acids present as propyl esters (see Experimental Section). The results are summarized in Table II. The significance of the results is considered in the section on the mechanism of the reaction.

Gas yields of selected runs are given in Table III. The gas law was used to calculate the yields from the glpc analysis of the gas from the reaction bulb void. The amount of product gas dissolved in the liquid phase was calculated from the estimated[22] solubilities of the gases in the isobutyl acetate. The only two significant gaseous products were carbon monoxide and hydrogen. Carbon dioxide was reported only in trace quantity.

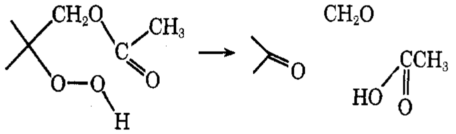
Proposed Mechanism.—It appears from the data presented here that isobutyl acetate oxidizes by the same mechanism as isobutane[11] but that subsequent decomposition of the product hydroperoxide complicates the overall picture. The following equations represent a minimum description of the system.



Except for the final two equations, all products are postulated to arise from attack at the tertiary hydrogen. Equations 4–7 are a straightforward analogy of the hydrocarbon oxidation mechanism.[1] The remaining equations require some elaboration and qualification.

Equation 8.—Decomposition of hydroperoxides[23] is usually thought to proceed *via* radical intermediates; yet the characteristics of this reaction seem to require, at least in part, a nonradical decomposition. Autocatalysis of the oxidation is very weak, which suggests that unimolecular or bimolecular decomposition to radicals is not obtained. An induced form of decomposition which would not result in a net generation of radicals as occurs with *tert*-butyl hydroperoxide[23] (eq 10 in part) cannot be a major contributor since little or no excess of **2** over the amount of hydroperoxide reduced is found. This conclusion is qualified on the assumption that peracids make no contribution to the hydroperoxide titer.

A brief investigation of the decomposition properties of the hydroperoxide was made by isolating (by distillation of unreacted IBAc) 1.46 mmol of **5**, adding IBAc until there was 40 ml of solution, and decomposing it at 120°. Within 16.25 hr, all of the hydroperoxide had decomposed, and 1.37 mol of acetone and 0.82 mol of acid had formed. More importantly, none of the acetate **2** was detected in the products. Thus, if radical **3** is formed, it rapidly fragments without competing abstraction from IBAc solvent to give **2**. Although we have no conclusive evidence, a cyclic transition state for decomposition looks attractive.



(8)

Equation 9.—Formic acid is a significant product of the reaction, and it seems reasonable to ascribe its formation to the oxidation of formaldehyde. The amount of formic acid found is significantly less than the amount of acetic acid; if formaldehyde and acetic acid are formed initially in equal amounts, conversion to formic acid is not quantitative. A possible explanation for this less than quantitative conversion is transesterification with the substrate to give isobutyl formate and acetic acid. Alternate reactions of formaldehyde include formation of peroxy acetals (with hydroperoxides) and subsequent decomposition. No significant levels of formaldehyde were detected by the chromotropic acid test during the oxidations or the hydroperoxide decomposition experiment. In run 16 (Table I) polarographic analysis of the water phase which separated on cooling gave some indication of formaldehyde. Another possibility for less than quantitative conversion of formaldehyde to formic acid could be the concomitant formation of carbon monoxide. Horner, Style, and Summer[24] studied the photooxidation of formaldehyde in the gas phase at 110° and found formic acid, carbon monoxide, carbon dioxide, and hydrogen as products. No analogous liquid phase studies seem to be available.

Equations 10–12.—As pointed out previously, an induced decomposition of the hydroperoxide does not seem to be the major pathway for its decomposition. A seemingly plausible alternate explanation for the formation of carbon monoxide, a significant product,

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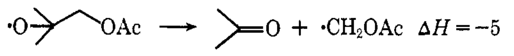
[22] Solubilities of 0.0088 and 0.0022 mol l.$^{-1}$ atm^{-1} for carbon monoxide and hydrogen, respectively, were calculated by the method of J. M. Prausnitz and F. H. Shair, *Amer. Inst. Chem. Eng. J.*, 682 (1961).

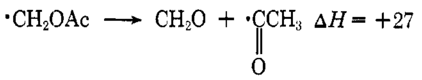
[23] R. Hiatt, T. Mill, and F. R. Mayo, *J. Org. Chem.*, **33**, 1416, 1421 (1968).

[24] E. C. A. Horner, D. W. G. Style, and D. Summers, *Trans. Faraday Soc*, **50**, 1201 (1954).

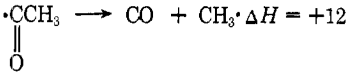
could be the decomposition of radical 3 (eq 11). However, a theoretical difficulty of eq 11 is the apparent endothermicity of the reaction. Calculation[25] of the thermodynamics of eq 11 suggests that the reaction is 34 kcal endothermic! If the reaction is broken down in steps the following results are obtained.



(11a)



$$\cdot CH_2OAc \longrightarrow CH_2O + \cdot C(=O)CH_3 \quad \Delta H = +27 \qquad (11b)$$

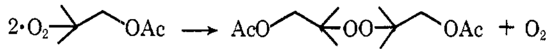


$$\cdot C(=O)CH_3 \longrightarrow CO + CH_3\cdot \quad \Delta H = +12 \qquad (11c)$$

These results suggest that the reaction may not proceed beyond the first step and that $\cdot CH_2OAc$ is degraded to carbon monoxide and other products *via* the associated peroxy radical $\cdot O_2CH_2OAc$. Reactions of this radical are not known.

Evidence that radical 4 does form includes the detection of small amounts of 2-oxopropyl acetate in the product mix. Thus, for this product to form, methyl instead of acetoxymethyl is cleaved from radical 4. The amount of 2-oxopropyl acetate formed is small, obscured in the glpc trace by acetic acid, and is estimated to be present in less than $^1/_{20}$ the amount of 2.

Equation 13.—As discussed in the section on rates, the termination reaction does not seem to be between two type 4 radicals.



Reactions of this type (between tertiary radicals) have relatively high activation energies,[26] and the overall rates of oxidation are sensitive to the addition[19] of small amounts of reactive substances. With the various fragments available from the decomposed hydroperoxide, a cross termination seems most likely.

Equations 12 and 13.—As mentioned in the introduction, it has usually been assumed that hydrogens α to an esterified hydroxyl function are inert to attack by peroxy radicals. Thus, ethylene dibenzoate could not be oxidized[8] at temperatures below 200°, and Mill[9] found isopropyl acetate quite resistant to oxidation but, perhaps, susceptible to water catalysis. The experiments with added water (run 16, Table I) or isobutyl alcohol (run 15, Table I) suggest that IBAc oxidation rates seem comparable to those of the "undoped" runs, and the acid yield of the run with isobutyl alcohol seems normal. Thus, rapid oxidation of the alcohol, relative to the oxidation rate of the ester, does not seem to be part of the mechanism. Hydrolysis of the ester apparently is slow; when the reaction mixture of run 16 (Table I) was cooled, water separated from the reaction in apparently the same amount started with. However, isobutyric acid is a significant product of the ester oxidation and needs to be accounted for. The most direct route to this product seems to be attack of the α position of the ester by some relatively reactive radical, most likely an alkoxy radical. Either decomposition of the ester radical as shown or, perhaps, degradation of the associated peroxy radical should ultimately lead to isobutyric acid.

Oxygen Balance.—The fact that secondary products are so prominent in the IBAc oxidation, even at 1% conversion, complicates accounting for the oxygen consumed. However, a reasonable approximation is to assume that the acetate 2 plus the acetone represent the total amount of hydroperoxide 5 originally formed. The difference between this amount of oxygen and the amount actually consumed represents the secondary oxidation processes, *e.g.*, conversion of formaldehyde to formic acid. Two quantities were determined in Table IV. The "excess oxygen" (ΔO_2) represents the oxygen available for secondary oxidation processes, and the "excess acid" (A_2) is the acid assumed to be present besides the acetic acid. Except for the first entry in the $A_2/\Delta O_2$ column, the ratio of "excess acid" to "excess oxygen" is ~2 and suggests the stoichiometry of eq 16.

TABLE IV

OXYGEN BALANCE FOR ISOBUTYL ACETATE OXIDATION[a]

Run	Acetone and diol	O_2	ΔO_2[b]	Acid − acetone = A_2[c]	$A_2/\Delta O_2$
			100°		
19	2.09	2.5	0.4	1.22	3.0
20	2.05	2.7	0.6	1.12	1.9
21	2.24	3.1	0.8	1.33	1.7
			120°		
1	3.94	5.6	1.7	3.26	1.9
3	2.09	2.8	0.7	1.23	1.8
7	4.37	4.9	0.5	1.10	2.2

[a] All quantities in millimoles. [b] "Excess oxygen." [c] "Excess acid."

$$2CH_2O + O_2 \longrightarrow 2HCOOH \qquad (16)$$

This treatment overlooks the formation of isobutyric acid as well as carbon monoxide and also predicts a 1:1 relationship between formic and acetic acid, a fact not borne out by the data of Table II.

Other Esters.—Preliminary experiments were carried out on isobutyl benzoate and isopentyl acetate. As expected, the oxidation behavior is mostly independent of the acid part of the ester. However, placing one more methylene group between the active hydrogen and the ester function causes the oxidation to more nearly resemble that of the hydrocarbon. Thus, isopentyl acetate oxidizes *ca.* five times as fast as isobutyl acetate, and the acid and gas yields are sharply reduced.

Registry No.—Isobutyl acetate, 110-19-0.

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[25] S. W. Benson, "Methods for the Estimation of Thermochemical Data," Wiley, New York, N. Y., 1968. The thermodynamics of eq 11c can be confirmed by the data of R. Walsh and S. W. Benson, *J. Phys. Chem.*, **70**, 3751 (1966).

[26] D. G. Hendry, *J. Amer. Chem. Soc.*, **89**, 5433 (1967).