19, 187-68-8; **20**, 209-86-9; **21**, 208-96-8; **22**, 209-42-7; **23**, 208-20-8; **24**, 4325-69-3; **25**, 13357-37-4; **26**, 13357-31-8; **27**, 257-56-7; **28**, 388-79-4; **29**, 31151-71-0; **30**, 217-04-9; **31**, 31151-73-2; **32**, 31180-51-5; **33**, 31151-74-3; **34**, 31151-75-4; **35**, 31151-44-7; **36**, 31151-45-8; **37**, 31141-14-7; **38**, 31141-15-8; **39**, 31141-16-9; **40**, 31141-17-0; **41**, 31141-18-1; **42**, 31141-19-2; **43**, 31141-20-5; **44**, 31141-21-6; **45**, 31141-22-7; **46**, 31141-23-8; **47**, 31141-24-9; **48**, 31141-25-0; **49**, 31141-26-1; **50**, 31141-27-2; **51**, 31141-28-3; **52**, 31141-29-4; **53**, 211-95-0; **54**, 20542-67-0; **55**, 20542-69-2; **56**, 20542-70-5; **57**, 31133-53-6; **58**, 5695-16-9; **59**, 4429-72-5; **60**, 20542-74-9; **61**, 569-40-4; **62**, 22719-10-4; **63**, 22719-09-1; **64**, 3526-04-3; **65**, 193-85-1; **66**, 781-30-6; **67**, 436-86-2; **68**, 22719-08-0; **69**, 22874-06-2; **70**, 187-78-0; **71**, 13357-45-4; **72**, 203-72-5; **73**, 194-32-1; **74**, 203-57-6; **75**, 203-71-4; **76**, 194-23-0; **77**, 193-90-8; **78**, 192-29-0; **79**, 31180-48-0; **80**, 31141-54-5; **81**, 31141-55-6; **82**, 31141-56-7; **83**, 31141-57-8; **84**, 31141-58-9; **85**, 31141-59-0; **86**, 31141-60-3; **87**, 31141-61-4; **88**, 31152-32-6; **89**, 31152-33-7; **90**, 31152-36-0; **91**, 31152-34-8; **92**, 31152-35-9.

Cobalt-60 Radiation-Initiated Oxidation of Hydrocarbons in Emulsion[1]

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Aqueous emulsions of a variety of hydrocarbons under cobalt-60 irradiation have been allowed to react with molecular oxygen at pressures of 1–4 atm at 50°. Unlike the effect observed in polymerization, emulsification of styrene had no significant effect on the oxidation rate or products as compared to that observed in hydrocarbon solution. With emulsions of styrene and α-methylstyrene, dependency on the rate of initiation and temperature is consistent with the bulk mechanism, and the product distribution qualitatively parallels bulk oxidations. Other hydrocarbons investigated include cyclohexene, cyclopentene, tetramethylethylene, tetralin, and cumene. The efficiency of initiation by radiation varied from 10 to 40%.

The effect of emulsification on the oxidation of hydrocarbons has received attention from a number of researchers, largely in the hope of finding an increase in the kinetic chain length or variation in products. The information available at the start of our program was inadequate to tell what the effect of emulsification was on any oxidation process. For example, studies have been made on methyl oleate,[3] methyl linoleate,[4] aldehydes,[5] cumene,[6] and 1,1-diphenylethylene,[6] but in these cases all experiments were performed without controlled initiation. Thus a comparison of rate with that in solution is not possible. The literature also contains many other articles reported in a phenomenological manner which contribute little to the understanding of emulsion oxidation.

Recently Hyde and Verdin[7] have reported on the effect of emulsification on the radiation-induced oxidation of methyl oleate under controlled conditions. Although hydroperoxide is formed quantitatively in the initial stages of the reaction in both emulsion and bulk, the yield of the hydroperoxide decreases more rapidly with conversion in the emulsion system than in bulk. The rate of emulsion oxidation, based on the amount of methyl oleate present, is increased up to a factor of 5.8 over the bulk rate. This increase is attributed to an increase in initiation rate and not to an enhancement in chain length. Apart from this small enhancement of rate, the reaction kinetics seem similar to those of the homogeneous system.

Using emulsion polymerization[8-12] as a model for emulsion oxidation one might expect that emulsification should cause rate enhancement. Briefly, the theory of emulsion polymerization[13,14] has utilized the concept of isolation of the chain carriers in the soap micelle or polymer particle, thereby preventing termination. Further rate enhancement occurs due to the high viscosity of the growing particle,[12] which retards diffusion-controlled termination within the particle even after another chain carrier enters the particle. Since the oxidation of hydrocarbons also follows a free-radical mechanism,[15,16] emulsification is expected to have an effect if the concept of isolation of the growing chain carriers is important. If the high viscosity of growing particles is the main factor which causes enhancement of rate in emulsion polymerization, then enhancement would be expected to be small in cases where the product is of a low molecular weight such that there is little change in the viscosity of the particle with conversion. In the oxidation of olefins which form alternating copolymers with oxygen, there may be sufficient changes in viscosity so that some rate enhancement might be expected to occur. There is only a limited amount of data on the emulsion oxida-

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tion of such compounds and then only for styrene,[17,18] where the results appear similar to that observed in bulk.[19,20] Thus our objective in studying emulsion oxidation has been directed largely, although not entirely, to the reaction of olefins which form polymeric products.

Most of the reactions have been initiated by γ radiation from cobalt-60. This source of initiation has distinct advantages over chemical initiation, as has been demonstrated in its use in emulsion polymerization.[21,22] Among the advantages are a constant and easily attenuated source of initiation and lack of chemical contamination.

Experimental Section

Materials.—Reactants and emulsifiers were obtained through the following sources: styrene, α-methylstyrene, cetyltrimethylammonium bromide (CTABr) and chloride (CTACl), *N,N*-bis(2-hydroxyethyl)dodecanamide (BHD), azobisisobutyronitrile, and cetylpyridinium chloride (CPC) from Eastman Organic Chemicals; cyclohexene, tetralin, cumene, acetaldehyde, potassium persulfate, and sodium lauryl sulfate (NaLS) from Matheson Coleman and Bell; cyclopentene and butadiene from Phillips Petroleum; tetramethylethylene from Aldrich; poly(oxyethylene) palmitate (POEP) from Atlas Chemical Industries; sodium laurate (NL) from Baker Chemical; methyl methacrylate from Rohm and Haas. *N*-(2-Diethylaminoethyl)palmitamide (P) was prepared from palmitoyl chloride and *N,N*-diethylethylenediamine and converted to the hydrochloride by treatment with hydrochloric acid. Hydrocarbons were distilled prior to use.

Apparatus.—Most oxidation and polymerization reactions were carried out in a thermostated bath constructed of $^3/_{16}$-in. sheet aluminum, which was placed by an aluminum window adjacent to one position of the cobalt-60 source. The reaction bulbs were clamped to the arm of a wrist action shaker so that when the source was in position the bulbs were at the position of maximum dose rate.

The reaction bulb was connected by Swagelok fitting (Nylon ferrules) to a valve joined by 20 ft of $^1/_{16}$-in. stainless steel tubing to an oxygen supply tank and pressure gauge located behind the radiation shield at ambient temperature. The total volume of the oxygen supply tank and connections to the valve was 42.5 ml. The volume (total) of the reaction bulb most commonly used was 160.5 ml. The radiation dose delivered to the bulbs was determined by ferrous sulfate dosimetry.

Procedure.—Emulsions were made up by dissolving the desired amount of emulsifying agent in 180 ml of water, then adding the desired amount of organic substrate to the soap solution and homogenizing the mixture in a high-speed blender for 1 min. The emulsion was poured into a capped jar to allow the foam to settle, and then 100 ml of the emulsion was delivered to the reaction bulb by hypodermic syringe; the bulb was weighed (to 1 mg) and then attached to the Swagelok fitting. If a polymerization rather than oxidation was to be followed, the bulb was capped with a serum stopper (rather than the fitting) so that samples could be withdrawn by a long hypodermic needle and syringe. Manipulation of an apparatus of this type has been described previously.[23] To avoid breaking emulsions no freeze–thaw degassing was carried out.

Calculations.—The pressure readings made at the ambient tank temperatures were corrected to 27° by the following equation

$$P_{27^\circ} = \frac{(14.7 + P_1)300.16}{(T_1 + 273.16)}Z$$

$$Z = \frac{V_1T_2 + V_2(273.16 + T_1) + RS(273.16 + T_1)T_2V_3}{V_1T_2 + V_2(300.16) + RS(300.16)T_2V_3}$$

where P_{27° is the corrected reading in psi absolute, P_1 is the measured pressure in psig, and T_1 is the ambient temperature. T_2 is the reaction temperature (of the bulb); V_1, V_2, and V_3 are the volumes of the apparatus (42.5 ml), void space in bulb (usually 60 ml), and emulsion volume (usually 100 ml); and R and S are the gas constant (0.08205 l. atm deg^{-1} mol^{-1}) and the solubility of oxygen in the emulsion, taken to be 15×10^{-4} mol l.$^{-1}$ atm^{-1} for most of the emulsions (styrene, 10% in water). The data were processed using a BASIC computer program and General Electric time-sharing computer service. Oxidation rates were calculated as described previously.[23]

Product Analysis.—In some oxidations, where polyperoxide and carbonyl compounds from substrate cleavage were present, products were isolated by delivering the 100-ml emulsion into 350 ml of methanol and allowing the mixture to stand in the refrigerator. The polymer settled out and the supernatant liquid was decanted and saved for glpc analysis. The polymer was redissolved in benzene and reprecipitated twice with methanol, then freeze-dried in benzene solution. The weight of the polymer and, in some instances, the molecular formula and molecular weight were determined.

Where polyperoxide was not expected as a major product, the emulsion was broken by addition of a strong solution of electrolyte, either ammonium sulfate or potassium sulfate, and this mixture was continuously extracted with ether. The ether solution was dried and worked up in a manner previously described[24] for determining products of oxidation of C_5, C_6, and C_7 hydrocarbons.

Results and Discussion

The following discussion of the results given in the tables shows that the kinetics and mechanism of emulsion oxidation much more closely follow bulk oxidation than emulsion polymerization phenomena. The discussion of an interesting "latex effect" (augmentation of oxidation rate of substrates when absorbed in a polymer latex) will be presented elsewhere.[25]

Emulsion Oxidation Rates *vs.* Bulk Rates.—In the following discussion the assumption that bulk oxidations follow the simplified rate expression (eq 1) is made.

$$R_0 = -\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t = k_\mathrm{p}[\mathrm{RH}](R_\mathrm{i}/2k_\mathrm{t})^{1/2} \qquad (1)$$

Here R_0 or $-\mathrm{d}[\mathrm{O_2}]/\mathrm{d}t$ is the rate of oxygen consumption, k_p is the rate constant for the propagation reaction

$$\mathrm{RO_2} + \mathrm{RH} \xrightarrow{k_\mathrm{p}} \underset{\text{(abstraction)}}{\mathrm{RO_2H}} \quad \text{or} \quad \underset{\text{(addition)}}{\mathrm{R\dot{O}_2RH}} \qquad (2)$$

where [RH] is the concentration of the substrate, R_i the rate of production of radicals in the system, and k_t the rate constant for the radical termination

$$2\mathrm{RO_2} \xrightarrow{k_\mathrm{t}} \text{nonradical products} + \mathrm{O_2} \qquad (3)$$

Equation 1, which is the simplest possible rate law for typical free-radical chain oxidation, requires that kinetic chain lengths be long and does not allow for complications that may arise,[12] such as nontermination[26] in eq 3. Nonetheless, it is a useful framework in which to discuss our results.

For a comparison of bulk oxidation rates with those observed in emulsion, the composite rate constant of eq 1, $k_\mathrm{p}/(2k_\mathrm{t})^{1/2}$, for various substrates has been collected next to the emulsion oxidation rates in Table III. It is apparent that the emulsion oxidation rates parallel the bulk rate only in a qualitative way which depends on

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TABLE I

OXIDATION OF STYRENE EMULSIONS AT 50°

Expt no.	Emulsifying agent, g/l. in aqueous phase[a]	C_8H_8, mmol	Time, min	ΔO_2, mmol	$R_0{}^b \times 10^4$, initial	$R_0{}^{b,c} \times 10^4$, final	Other data
				Co-60 Radiation at 200 rad/min			
9056-3	POEP 2.77	87.1			0.72		
44	POEP 5.56	86.3	1409	13.7	1.1	0.4^d	
130	POEP 5.53	87.8	2511	4.6	$<0.05^d$	0.2^d	First 1154 min to check for initial thermal rate; 1.878 g, $C_8H_{8.28}O_{1.89}$, mol wt ~3500, isolated
139a	POEP 11.5	86.6	~4000	16.0	1.4	1.5	
18	POEP 5.62 NLS 1.47	87.7	1379	16.7	0.93	1.9 0.9^d	
22	$POEP^e$ 51.1	339.2	435	1.5	0.04^d 0.16	0.24	
69	CTABr 5.56	87.5	1408	9.9	0.9	0.8	
72	CTABr 11.2	~88	1133	5.0	1.0	0.1	Emulsion broken at end of run
102	CTABr 5.7	87.4	1513	6.0	0.58^d 1.1	0.6^d	
107	CTACl 5.73	86.3	254	10.1	0.42^d 1.2	1.2^d	
15	CPC 5.57	84.3	2510	7.7	0.40	0.33	
105	NLS 5.88	88.4	395	1.7	0.81	0.2^d	
79	BHD 5.56	89.4	1219	8.6	1.3	0.8	Emulsion broken at end of run
97	*e* *e*	400	1180	5.0	0.08^d 0.22	0.13^d	
9216-18	POEP 5.55 NLS 1.42	87.7	1336	15.9	0.90	1.9	
9056-53	POEP 5.49	95.7	76	0.0	82^f		
				$K_2S_2O_8$ Added as Initiator, No Irradiation			
							$K_2S_2O_8{}^g$ concn, *M*
9056-11	POEP 5.53	88.8	1280	2.7	0.34		0.0011
125	POEP 5.56	84.2	4068	78.7	3.1	2.8^h	0.0057
110	POEP 5.56	89.8	372	7.7		2.0	0.0110
116	POEP 5.80	85.3	1150	31.5	3.3	3.7	0.0219
139a	POEP 11.5	84.1			1.4		0.0012
b	POEP 11.5	84.1^c			2.0^c		0.0023
c	POEP 11.5	84.1^c			2.9^c		0.0045
8	POEP 11.0	86.3	400	14.8	4.4	4.4	0.0108
133	POEP 5.6 NLS 1.4	88.8	187	11.1	7.0	7.0	0.011
136	POEP 5.53 NLS 2.76	87.5	1233	47.7	7.0	2.3	0.011
6	POEP 5.53	89.8	1450	3.4	0.27	0.27	[ABN] = 0.010 in C_8H_8; no $K_2S_2O_8$ in H_2O

[a] POEP = $C_{15}H_{31}COO(CH_2CH_2O)_{20}H$; CTACl = $C_{16}H_{33}N(CH_3)_3Cl$; NLS = $C_{12}H_{25}OSO_3Na$; CTABr = $C_{16}H_{33}N(CH_3)_3Br$; BHD = $C_{11}H_{23}CON(C_2H_4OH)_2$; CPC = $C_{16}H_{33}N(CH)_5Cl$; NL = $C_{11}H_{23}COONa$; P = $C_{15}H_{31}CONHCH_2CH_2NH(C_2H_5)_2Cl$. All runs done with *ca.* 90 ml of H_2O present; O_2 pressures ranged from 1 to 4 atm. [b] Initial and final rates in mol of O_2 per mol of styrene per min. [c] Based on starting quantity of styrene. [d] Thermal rate, no radiation. [e] Neat styrene, no aqueous phase. [f] Rate of polymerization in absence of oxygen. [g] Concentration in the aqueous phase. [h] Average rate from 6 to 83% conversion.

the emulsifying agent. For those hydrocarbons that oxidize by the abstraction process, where hydroperoxide products may augment the initiation, the discrepancies are even more marked.

The last column of Table III, which is reassembled from Tables I and II, gives a value expected to reflect the efficiency of capture of radicals from the aqueous phase by the droplets of the substrate. The number was obtained by calculating R_i from eq 1

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

and dividing by the total initiation rate produced by the Co-60 radiation of 200 rads/min. The latter initiation rate for the oil phase, assuming that all radicals formed in the aqueous phase enter the oil phase, is calculated to be 1.0×10^{-5} *M*/min in the case where the volume ratio of water to hydrocarbon is 9 to 1. A value[27] of $G(R\cdot) = 5$ was taken for water, and radicals produced by the direct radiolysis of the hydrocarbon were neglected. Assuming that the value for α-methylstyrene is too low because of transfer, and neglecting the anomalous tetramethylethylene result, capture of radicals by the substrate droplets appears 10–40% efficient where the concentration of emulsifying agent is 6.0 g/l. of H_2O and the volume ratio of substrate to water is 1:9. Since these numbers are calculated from eq 1 derived for the bulk mechanism, they are expected to be on the high side if there is any intrinsic acceleration of oxidation in emulsion. Hyde and Verdin concluded, on the basis of inhibited emulsion oxidation of methyl oleate, that capture of radicals from the aqueous phase was 100% efficient.[7]

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TABLE II

OXIDATION OF HYDROCARBONS IN EMULSION AT 50° Co-60 RADIATION INITIATION (200 RADS/MIN)

Expt no.	Hydrocarbon	Emulsifying agent, g/l.[a]	RH, mmol	ΔO_2, mmol	$R_0 \times 10^4$, initial[b]	$R_0 \times 10^4$, final[b,c]	Other data
9056-113	α-Methylstyrene	CPC 11.1	79.7	3.4	0.78	0.4	Initial thermal rate ~0.09
120		CPC 11.3	67.4	1.5	0.20	0.1	98.1 mmol of C_6H_6 present
94		CPC 5.56	77.2	4.7	0.36		
82		BHD 5.40	75.2	8.6	2.6	0.9	Emulsion broken
9216-65		POEP 5.53	77.7	12.7	1.2	1.5	
9056-49	Cyclohexene	POEP 5.95	96.8	10.7	0.65	1.3	8.3 mmol of $-O_2H$ formed
65		NL 5.12	97.4	11.4	0.14	1.0	
74		P 5.6	98.4	5.3	0.15	0.79	
56	Cyclopentene	POEP 6.02	114.2	11.9	0.28	1.0	
86	$Me_2C{=}CMe_2$	CPC 5.67	82.7	9.0	0.11	2.0	
9413-12		POEP 5.50	79.6	17.3	2.0	2.0	
9216-104	Tetralin	POEP 5.51	76.4	2.1	0.70	0.8	
9413-24	Butadiene	POEP 5.0	101.3	9.2	0.90	0.82	
9216-71	Cumene	BHD 5.61	74.6	1.1		0.10	
9413-26[d]		NLS 5.52	74.9	5.4	0.1	0.65	

[a–c] Same significance as in Table IV. [d] pH of aqueous phase initially adjusted at ~9.

TABLE III

OXIDATION OF HYDROCARBONS IN EMULSION AND BULK AT 50°

	Emulsifying agent					
	CPC		POEP			
Hydrocarbon	Concn[a]	R_0[b]	Concn[a]	R_0[b]	$k_p/(2k_t)^{1/2}$ bulk[c]	Efficiency of radical capture[d]
α-Methylstyrene	5.6	0.36	5.5	1.2	0.196 (2.2)	0.04
Styrene	5.6	0.40	5.5	1.0	0.088 (1.0)	0.15
$Me_2C{=}CMe_2$	5.7	0.11	5.5	2.0	0.067 (0.7)	0.87
Cyclohexene			5.9	0.65	0.027 (0.3)	0.49
Cyclopentene			6.0	0.28	0.035 (0.4)	0.07
Tetralin			5.5	0.70	0.033 (0.4)	0.43
Butadiene			5.0	0.90	0.093 (1.1)	0.11

[a] Grams of emulsifier/liter of H_2O. [b] 10^4 mol of O_2 per mol of RH per min. [c] $(M\ \text{min})^{-1/2}$, from D. G. Hendry, *Advan. Chem. Ser.*, **75**, 24 (1968); F. R. Mayo, M. G. Syz, T. Mill, and J. K. Castleman, *ibid.*, **75**, 38 (1968); D. E. Van Sickle, F. R. Mayo, R. M. Arluck, M. G. Syz, and E. S. Gould, *J. Amer. Chem. Soc.*, **89**, 967, 977 (1967). [d] For POEP runs; see text for calculation.

For the single substrate, styrene, the data of Table I show that the radiation-induced oxidation rate is slightly dependent on emulsifier type. At the most commonly used concentration of emulsifying agent, 5.5 g/l., only *N*,*N*-bis(2-hydroxyethyl)dodecanamide (BHD) seems to give a slight rate enhancement (expt 9056-79). Cetylpyridinium chloride (CPC) emulsifying agent (expt 9056-15) apparently produces a 60% retardation[28] in rate compared to the average, and sodium lauryl sulfate (NLS) seems to be mildly rate retarding (expt 9056-105). There does not seem to be any clear rate distinction between anionic, cationic, and nonionic emulsifiers. Part of the effect of emulsifying agent may be that of a transfer agent that provides a more rapid termination reaction in the substrate droplet than would occur with pure hydrocarbon.

Data are less complete for substrates other than styrene, but the general effect of emulsifier type seems to be maintained (Table II). α-Methylstyrene demonstrates the most significant dependence of oxidation rate on emulsifier type. With CPC emulsifier[28] (expt 9056-94), the rate is one-sixth to one-seventh of that observed with BHD emulsifier (expt 9056-82); the rate with POEP is intermediate. With α-methylstyrene as substrate, the transfer effect mentioned above could be expected to effect a significant rate change, since the termination constant for termination between the peroxy radical from the emulsifying agent and the α-methylstyrene polyperoxy radical is expected to be 10 to 100 times as fast as the usual termination for pure α-methylstyrene.[29]

The fundamental rate difference[17] between emulsion polymerization and emulsion oxidation of styrene was confirmed (expt 9056-53, Table I). Our results show that R_p/R_0 is 100 instead of 1000; the latter result was obtained with persulfate initiator. In bulk[18] at constant R_i, $R_p/R_0 = 1.7$. Interception of the polymerization with oxygen at any stage of conversion (at least to 50%) brought about the abrupt rate diminution, although the subsequent rate was subject to an enhancement due to the polymer latex present.[25] As far as could be determined, the interception of polymerization was complete with 1 atm of oxygen over the emulsion and the subsequent oxidation rate was unchanged by raising the pressure as high as 6 atm.

Effect of Emulsifier and Substrate Concentration.—Data that indicate the effect of emulsifier and substrate concentration on the rate of oxidation of styrene and α-methylstyrene are gathered in Table IV. In-

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(28) Quaternized pyridine derivatives may show unusual reactivity with peroxy radicals, hydroperoxides, or at least hydrogen peroxide: D. W. Bristol and D. C. Dittmer, *J. Org. Chem.*, **35**, 2487 (1970).

(29) K. U. Ingold, *Accounts Chem. Res.*, **2**, 1 (1969).

TABLE IV

EFFECTS OF EMULSIFIER AND SUBSTRATE CONCENTRATION, TEMPERATURE, AND DOSE RATE ON STYRENE AND α-METHYLSTYRENE EMULSION OXIDATION[a]

POEP concn, g/l. in aqueous phase	Substrate concn, mol/l. of H_2O	R_0[b] × 10^4, initial	[ΔO_2], mol/l. of H_2O	R_0[b] × 10^4, final	Efficiency of radical capture[c]
		Styrene			
62.3	0.97	3.5	0.050	3.8	1.6
27.8		1.7	0.75	1.7	0.37
27.2		1.7	0.049	1.4	0.37
11.5		1.4	0.18	1.5	0.25
5.53		1.0	0.051	0.2[d]	0.13
2.77		0.6	0.11	0.72	0.046
6.20	2.16	0.84 (1.82)			0.20
5.95	1.52	0.91 (1.38)			0.18
5.67	0.962	1.10 (1.06)			0.16
5.26	0.455	2.3 (1.05)			0.30
5.09	0.221	3.4 (0.75)			0.30
5.00	0.044	11.0 (0.48)			0.27
5.53 (60°)	0.97	1.3	0.16	1.5	
5.53 (30°)		0.59			
5.52 (18°)		0.28			
5.5 (1°)		0.09			
5.53[e]		0.63	0.10	0.92	
5.53[f]		0.45			
27.8[e]		1.3_8	0.14	1.4	
27.8[f]		0.7_8			
		α-Methylstyrene			
5.5[e]	0.885	0.65	0.10	0.92	
5.5[f]	0.889	0.42	0.070	0.7	
5.5	0.855	1.2 (1.03)			0.04
5.09	0.197	3.6 (0.71)			0.07
		Blank Run			
5.00		(0.18)			

[a] Emulsifying agent is poly(oxyethylene) palmitate in all runs, dose rate is 200 rads/min, and temperature is 50° unless otherwise noted. [b] Rate of oxidation in mol of O_2 per mol of substrate per min; rates in parentheses are in mol of O_2 per l. of H_2O per min. [c] See text for calculation. [d] Thermal rate. [e] Dose rate: 79 rads/min. [f] Dose rate: 43 rads/min.

creasing emulsifier concentration increases oxidation rate and, for the styrene–POEP system, a plot of log [R_0] *vs.* log [POEP] (as weight per cent in the aqueous phase) gives a straight line with some scatter at the higher POEP concentrations. The slope of the line is very nearly $^1/_2$. The expected order of emulsion polymerization rates with respect to emulsifier concentration is $^3/_5$ according to the Smith–Ewart theory.[4] However, in view of the one-half-order dependence of oxidation rate on initiation rate, *i.e.*, dose rate, we do not take this emulsifier order to indicate that the emulsion polymerization rate laws apply. The total effect of increased emulsifier concentration is expected to arise from several factors, including finer division of the substrate, altered composition of the substrate (changing the feed composition of a cooxidation), and more solubilization[5] of the substrate. The first and second effects are expected to be rate enhancing and the third retarding.

In Table IV data for the oxidation of styrene and α-methylstyrene at various concentrations show that the specific rate [mol of O_2 (mol of RH)$^{-1}$ min^{-1})] increases as the amount of styrene is decreased. Part of the increase is due to the reaction of emulsifying agent, as can be seen by comparing the rate [mol of O_2 (l. of $H_2O)^{-1}$ min^{-1}], where the styrene was 0.044 *M*, with the rate where there was no styrene. Here approximately one-third of the oxygen consumption is due to emulsifying agent. At higher styrene concentrations the contribution is much less. The efficiency at which radiation results in initiation has been calculated as before and listed in the last column on Table IV. Except for the highest and lowest POEP concentrations, efficiencies are in the same range as previously found.

Effect of Dose Rate on Oxidation Rate.—The results of several emulsion oxidations done at different radiation dose rates are shown in Table IV. A plot of log rate *vs.* log dose rate shows that, for styrene at each emulsifier concentration, the order of the reaction with respect to dose rate is 0.5. The numbers actually observed are 0.45 (27.8 g of POEP/l.) and 0.50 (5.53 g of POEP/l.), which are assumed to be identical within experimental error. The one-half-order dependence indicates that exchange of radicals between the droplets and the aqueous phase is rapid at either emulsifier concentration and that bimolecular termination re-

TABLE V

EMULSION OXIDATION PRODUCTS[a]

Expt no.	Substrate	Emulsifying agent, g/l. of H_2O	Conversion, %	Time, min	Products	Yield,[b] %
9056-139	Styrene	POPE 11.5	11.9	4000	Polyperoxide[c]	81
9216-65	α-Methylstyrene	POEP 5.5	16.4	1070	Polyperoxide[d]	65
					Acetophenone	22
9216-104	Tetralin	POEP 5.5	3.1	486	Hydroperoxide[e]	93
9216-100	Tetralin	POEP 5.5	13.7	2490	Hydroperoxide[e]	58
9216-116	Tetralin[f]	None	2.7	885	Hydroperoxide[e]	91
			10.6	2440	Hydroperoxide[e]	85
			14.5	3950	Hydroperoxide[e]	89
9056-86	Tetramethylethylene	CPC 5.6	10.9	1360	Hydroperoxide[g]	42
9056-56	Cyclopentene	POEP 5.5	11.2	1360	Hydroperoxide[h]	92
9216-140	Acetaldehyde[i]	None	12.8	1250	Acid[i]	98
					Peracid[e]	2
9216-148	Acetaldehyde[i,j]	None	29.0	1120	Acid[i]	95
9413-26	Cumene[k]	NLS 5.5	7.2	1440	Hydroperoxide[k]	3

[a] At 50°, dose rate 200 rads/min. Emulsion of 10 ml of substrate and 90 ml of H_2O except as noted; oxygen pressure ~4 atm. [b] Yield based on moles of substrate consumed (≅oxygen consumed). [c] Mol wt 3500; analyzed $C_{8.0}H_{8.3}O_{1.9}$. [d] Mol wt 5500; analyzed $C_{9.0}H_{10.2}O_{2.0}$. [e] Determined by titration, tetralin hydroperoxide. [f] Pure tetralin, initiation by 0.025 *M* ABN at 45°. [g] Mixture of 1-hydroperoxy-2,3-dimethyl-2-butene and 3-hydroperoxy-2,3-dimethyl-1-butene; other products detected were 14% residue, 4.5% acetone, and 2.2% tetramethylethylene epoxide. [h] Cyclopentene 3-hydroperoxide. [i] 1.0 *M* dissolved in water, acid product is acetic acid, peracid product is peracetic acid. [j] Initiation by 0.1 *M* $K_2S_2O_8$. [k] Basic emulsion, initial pH ~9; titrated product cumene hydroperoxide.

sults. This is in contrast to emulsion polymerization phenomena where, by the Smith–Ewart theory, the number of particles forming (and thus the rate) in the initial stages of the reaction is proportional to the two-fifths power of aqueous phase initiation.[4] In the latter stages of polymerization, the dependence on dose rate theoretically drops to zero, although in practice some initiation is required to maintain the polymerization rate.[30] According to the review of Stannett, *et al.*,[22] the two-fifths order expected in polymerization rate is not easily confirmed experimentally, and numbers ranging from 0.22 to 0.5 have been reported. For oxidation of methyl oleate, a substrate that reacts by an abstraction mechanism, Hyde and Verdin[7] report a reaction order of 0.5 with respect to dose rate. It is interesting that, in emulsion oxidation of styrene, the initiation rate order is close to the ideal bulk value of 0.5, while in bulk, a mechanistic anomaly causes the experimental order to be 0.6.[31]

The dose rate dependence of α-methylstyrene emulsion oxidation is significantly higher than 0.5. The usual log–log plot of the data gives a straight line of slope 0.63. A dependence of 0.5 is observed in the bulk phase. This change may be due to the transfer with POEP emulsifying agent, as described in an earlier section. Kinetic analyses[32] of fully inhibited systems show first-power dependence on initiation rate.

Where initation was by potassium persulfate (expt 9056-139 of Table I), the apparent order with respect to persulfate concentration is 0.56. Complication[33] in the decomposition kinetics of potassium persulfate obscures the significance of this result. That the decomposition of potassium persulfate in aqueous solution is strongly influenced by minor changes in the medium is illustrated by comparison of oxidation rates of expts 9056-130, -110, -133, and -136 and 9416-18 of Table I. Addition of sodium lauryl sulfate to POEP-emulsified styrene in potassium persulfate solution increased the rate of oxidation from 2.6 to 7.0 × 10^{-4} mol (mol^{-1} min^{-1}). Addition of sodium lauryl sulfate to radiation-induced emulsion oxidations did not affect the rate.

Effect of Temperature on Emulsion Oxidation Rate.—Data for experiments at different temperatures in Table IV were used for preparing an Arrhenius plot to determine the overall activation energy of the emulsion oxidation process. The points seem to define two lines, one from 30 to 60° of slope, corresponding to an activation energy of 5.6 kcal/mol, and another from 1 to 30°, indicating an activation energy of 10.6 kcal/mol. However, the statistical line for all the points yields an activation energy of 8.6 kcal/mol, which corresponds precisely with the reported value for bulk styrene oxidation.[34] The energy of activation for the production of radicals from the radiolysis of water is assumed to be zero. The energy of activation for radiation-initiated emulsion polymerization of styrene was recently found[22] to be 3.6 kcal/mol, in agreement with the pioneering work of Ballantine,[21] although in bulk a value of 8.2 kcal/mol is found.[35]

Products from Oxidation of Emulsions.—The products reported for the oxidations of the emulsions in Table V are qualitatively consistent with the results obtained for the corresponding oxidations in the bulk. The 81% yield of styrene polyperoxide is comparable to the 95% yield for the bulk reaction,[18] while the 65% yield of poly-α-methylstyrene peroxide compares with an expected value of 81%.[36] The lower yields may arise from a lower effective concentration of oxygen in the emulsion system than in the bulk. In each case the yields correspond with the results in bulk expected near 1 atm of oxygen, or slightly lower, rather than 4 atm, at which the emulsion reactions were run. However,

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[33] C. E. M. Morris and A. G. Parts, *Makromol. Chem.*, **119**, 212 (1968).

[34] J. A. Howard and K. U. Ingold, *Can. J. Chem.*, **43**, 2729 (1965).

[35] Reference 16, p 84.

[36] F. R. Mayo and A. A. Miller, *J. Amer. Chem. Soc.*, **80**, 2480 (1958).

the lower yields may also reflect the increased difficulty in isolating products from emulsions, or in part of the oxygen being present as oxidized emulsifier. The molecular weights of these polyperoxides from emulsion oxidations are comparable to bulk oxidation products.

The comparison of yield of tetralin hydroperoxide in emulsion and in bulk oxidation (initiated by azobisisobutyronitrile) indicates that the yield drops off with conversion faster in emulsion. Hyde and Verdin[7] observed the same phenomenon with methyl oleate. The hydroperoxide yields in the emulsion oxidation of tetramethylethylene and cyclopentene are nearly identical with those observed in the bulk.[23,24] In the case of tetramethylethylene, the analysis for acetone is complicated by the high solubility of acetone in the aqueous phase. While the conversion of cumene to cumene hydroperoxide is reportedly favorable in thermally initiated basic emulsions,[37] our radiation result gave a very low hydroperoxide yield.

Registry No.—Cobalt-60, 10198-40-0; α-methylstyrene, 98-83-9; cyclohexene, 110-83-8; cyclopentene, 142-29-0; tetramethylethylene, 563-79-1; tetralin, 119-64-2; butadiene, 106-99-0; cumene, 98-82-8; styrene, 100-42-5.

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The Chemistry of Carbanions. XX.
A Comparison of α-Chloro Enolate Anions and α-Diazo Ketones[1a]

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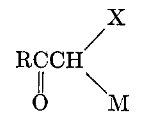
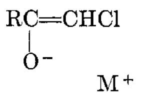
The α-chloro ketones, 2-chlorocyclohexanone (**5**), chloromethyl cyclohexyl ketone (**7**), and phenacyl chloride (**13**), have been converted to the corresponding enol acetates and trimethylsilyl enol ethers. These enol derivatives have served as precursors for the corresponding lithium α-chloro enolates **6**, **8**, and **16** which are stable intermediates. Even the addition of copper(I) compounds or the formation of α-mercuri derivatives of these enolates does not promote their decomposition to α-ketocarbenes. In contrast, the α-diazo derivatives **17** and **21** of acetophenone and methyl cyclohexyl ketone are readily decomposed by added copper(I) derivatives. The soluble complex, $(n\text{-Bu}_2\text{S})_2\text{CuI}$, is an especially convenient catalyst for the decomposition of these α-diazo ketones, compound **21** being rapidly decomposed in solution at 5-10°. With small amounts of this catalyst and excess olefin the norcarane derivative **22** was the major product. With an equimolar amount of this catalyst, the keto sulfide **26** (believed to arise from a sulfur ylide intermediate) became the major monomeric product.

To pursue further the idea[2] that the copper-catalyzed reactions of α-diazo carbonyl compounds may involve copper(I) derivatives such as structure **1a** which possess a good leaving group ($N^+{\equiv}N$) at the α position, we have investigated the behavior of certain metal derivatives of α-chloro enolate ions (**2**). We wished to learn whether certain of these materials (*e.g.*, **1b** or **2**) would show either behavior similar to the copper (I)-diazo ketone reagent or the behavior expected of an α-keto carbene **3**. The metal enolates of α-halo esters and α-halo ketones have served as intermediates in a number of synthetically useful reactions such as the Darzens glycidic ester condensation and related reactions,[3,4] the formation of cyclopropane derivatives by Michael additions involving α-chloro enolates,[5] and the reaction of α-bromo enolates with trialkylboranes.[6] In all of these cases, it is probable that the metal α-halo enolates (*e.g.*, **2**) and not the α-keto carbenes **3**, which might be formed from the enolates, are the actual reactants. Further evidence in support of the view that α-halo enolate anions (*e.g.*, **2**) are not rapidly converted to α-keto carbenes **3** has been obtained by the formation and subsequent acylation of several α-halo enolates to form α-halo enol esters[7-9] such as **4**. In the present study we have generated several metal α-chloro enolate anions **2** from either enol acetate[10] or trimethylsilyl enol ether[11,12] precursors.

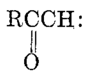


1a, X = $\overset{+}{N}{\equiv}N$, M = Cu
b, X = Cl



$\mathrm{RC(O^-)}{=}\mathrm{CHCl}\;\; M^+$

2



$\mathrm{RC({=}O)CH{:}}$

3

Preparation of Lithium α-Chloro Enolates.—The most successful of previous preparations[7-9] of α-chloroenol esters have involved acylation of the inter-

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