bromide titrated with thiocyanate by the Volhard method. The proper ratio (1:1) of bromide to cyanide was found.

Anal. Found: Br, 40.4, 40.0; CN, 12.97, 12.84.

Determination of halogen in a similar sample (n^{20}D 1.4437; d^{20}_{20} 1.285; M^{20}D 36.80) by means of sodium in liquid ammonia[19] gave the same halogen analysis, indicating that the hydrolysis above was quantitative.

Anal. Found: Br, 39.9, 41.0.

In three of the seven addition reactions, an appreciable portion (*ca.* 20%) of the hydrogen bromide addition product boiled at a considerably higher temperature (b. p. 83° (14 mm.), 65° (4 mm.)) and had a considerably higher index of refraction (n^{20}D 1.4618–1.4697). These are properties which correspond to β-bromo-α-ethoxyacrylonitrile.

When about two moles of hydrogen bromide was passed into α-ethoxyacrylonitrile a light tan powder separated. This material was insoluble in ether but dissolved readily in water, forming a solution which reduced silver nitrate to silver. The powder was washed with ether, dried and analyzed.

Anal. Calcd. for $C_5H_8NOBr \cdot HBr$: Br, 61.72. Calcd. for $C_5H_8NOBr \cdot 2HBr$: Br, 71.48. Found: Br, 67.1, 68.3, 66.6.

The average of these halogen analyses, 67.4%, corresponds to 1.48 moles of hydrogen bromide per mole of bromonitrile.[15]

This same powder precipitated from distilled samples of either α- or β-bromo-α-ethoxypropionitrile on standing, even in a dry-ice–acetone bath in the case of the α-isomer. Evidently the bromonitrile was slowly converted to the unsaturated nitrile by loss of hydrogen bromide which then combined with more of the bromonitrile to yield the insoluble nitrile hydrobromides.

Hydrolysis of α-bromo-α-ethoxypropionitrile (III) proceeded vigorously when water was added or when the nitrile was poured into water. The essentially quantita-

(19) Vaughn and Nieuwland, *Ind. Eng. Chem., Anal. Ed.*, **3**, 274 (1931).

tive progress of the hydrolysis is indicated by the analyses above for halogen and cyanide on an alkaline hydrolysis mixture. The presence of cyanide ion was further proved by the formation of a copious precipitate of Prussian blue. When a sample of α-bromo-α-ethoxypropionitrile (2 g.) was carefully hydrolyzed by dropwise addition of water at 0°, the hydrolysis mixture extracted with ether, dried and distilled, a few tenths of a cubic centimeter of liquid with the characteristic odor of ethyl acetate was obtained, b. p. 75–90°, n^{19}D 1.3728. The corresponding properties for ethyl acetate are b. p. 77°, n^{19}D 1.3722.

A 10-g. sample of the bromonitrile was hydrolyzed with cold alkali and a small portion distilled. Treatment of the distillate with 3,5-dinitrobenzoyl chloride yielded a small amount of crystals, m. p. 89°. Ethyl 3,5-dinitrobenzoate melts at 93°.[20] The alkaline hydrolysis mixture was then acidified with phosphoric acid and distilled. The distillate was neutralized with sodium hydroxide and treated with *p*-bromophenacyl bromide.[20] A copious precipitate of the *p*-bromophenacyl ester of acetic acid was obtained, m. p. 84–85°.[20]

Summary

α-Ethoxyacrylonitrile has been prepared from α,β-dibromoethyl ethyl ether by treatment with cuprous cyanide followed by dehydrohalogenation.

Addition of hydrogen bromide to α-ethoxyacrylonitrile yielded principally α-bromo-α-ethoxypropionitrile, indicating that the ethoxyl group was a more potent factor than the nitrile group in directing addition to the carbon–carbon double bond.

Attempts to polymerize α-ethoxyacrylonitrile by aqueous potassium persulfate, by aluminum chloride and by benzoyl peroxide and ultraviolet light failed.

(20) Shriner and Fuson, "Systematic Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940.

URBANA, ILLINOIS RECEIVED JUNE 27, 1941

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

The Mechanism of the Peroxide-Catalyzed Polymerization of *d-s*-Butyl α-Chloroacrylate[1]

BY CHARLES C. PRICE AND ROBERT W. KELL

The kinetics of the benzoyl peroxide-catalyzed polymerization of *d-s*-butyl α-chloroacrylate have been investigated in dilute dioxane solution at several temperatures between 26 and 68°, making use of the polarimetric technique for following the polymerization recently reported by Marvel, Dec and Cooke.[2] The reaction proceeded smoothly under these conditions and the rate

(1) Presented before the division of Organic Chemistry at the St. Louis meeting of the American Chemical Society, April 9, 1941.
(2) Marvel, Dec and Cooke, THIS JOURNAL, **62**, 3499 (1940).

could be conveniently and accurately followed by this method since the specific rotation of the monomer was twice that of the polymer.

The *d-s*-butyl α-chloroacrylate was prepared according to the directions of Marvel, Cooke and Dec,[2] b. p. 70–71° (23 mm.), n^{20}D 1.4360. It was stored over hydroquinone and samples were twice redistilled immediately before use since the uninhibited monomer polymerized appreciably in a few days at room temperature. Two samples

of the benzoyl peroxide[3] used were dissolved in acetone and treated with aqueous potassium iodide; titration of the iodine liberated indicated that the peroxide was essentially pure (99.92 and 99.86%). Standard solutions of the monomer and the peroxide in pure dry dioxane[4] (b. p. 101.4°; m. p. 11.67°) were prepared in volumetric flasks and were mixed in various ratios in sufficient volume to fill 1-dm. jacketed polarimeter tubes. Water from a thermostat regulated to ±0.2° was circulated through the jacket around the tubes and the rotations of the reaction mixtures were observed at specified intervals.

On the basis of the assumption that the specific rotation of the monomeric units in the polymer chains is independent of the degree of polymerization, the concentration of monomer in the reaction mixture is obtained as follows

$$[M]_t = [M]_0 \frac{\alpha_t - \alpha_\infty}{\alpha_0 - \alpha_\infty}$$

In this expression, $[M]_0$ is the initial monomer concentration, $[M]_t$ that at time t, α_0 is the observed initial rotation, α_t that at time t, and α_∞ the final rotation when the polymerization is complete. The observation that the specific rotation of the polymer is approximately half that of the monomer[2] has been substantiated since the rotations of the various reaction mixtures reached a constant value, α_∞, 51 ± 2% that of α_0.

A measurement of the peroxide remaining in a polymerization mixture after a period of twelve hours at 52° and eighteen hours at room temperature showed a decrease of 24%.[5] Since the reaction was 75% complete in six hours, the concentration of catalyst may be considered to have remained essentially constant for the major portion of the reaction.

Results.—The measurements of the benzoyl peroxide-catalyzed polymerization of d-s-butyl α-chloroacrylate in dilute dioxane solution have clearly demonstrated the rate of the reaction to be proportional to the monomer concentration ($[M]$) and to the square root of the catalyst concentration ($[Cat]$). This relationship obtained over a wide range in the ratio of the initial concentrations and for practically the entire course of the polymerization.

$$-d[M]/dt = k[Cat]^{1/2}[M] \tag{1}$$

(3) Lucidol Corporation, Buffalo, New York.

(4) Oxford, Biochem. J., 28, 1325 (1934); Scatchard and Benedict, THIS JOURNAL, 58, 837 (1936).

(5) This observation conforms with the report by Brown[3] that benzoyl peroxide was decomposed to the extent of 50% in about eight hours at 80° in benzene solution.

Since the benzoyl peroxide concentration was found to remain essentially constant during the major portion of the polymerization, the equation takes the integrated form

$$-\ln[M]_t = k't + const.$$

or

$$\ln \frac{[M]_0}{[M]_t} = k't \tag{2}$$

In equation (2), $[M]_0$ represents the initial concentration of monomer, $[M]_t$ that at time t, and $k' = k[Cat]^{1/2}$. The logarithm of the ratio of initial monomer concentration to that at time t, as determined polarimetrically, was then plotted against the time in hours. The slopes of the straight lines so obtained gave the values of k' for the various experiments. The rate constants, k, were then calculated by dividing k' by the square root of the benzoyl peroxide concentration. The values for k' and k obtained in this manner are summarized in Table I.

TABLE I

KINETICS OF THE BENZOYL PEROXIDE-CATALYZED POLYMERIZATION OF d-s-BUTYL α-CHLOROACRYLATE IN DIOXANE SOLUTION

| $[M]^a$	$[Cat]^a$	k'	k	k (av.)
		Temp., 26°C.[b]		
5.63	2.00	0.0194	0.0137	
5.82	1.67	.0155	.0120	0.0135 (±6%)
7.09	2.67	.0229	.0140	
4.15	3.20	.0257	.0143	
		Temp., 44°C.		
5.83	4.01	.100	.0515	
8.74	4.58	.112	.0533	0.0515 (±2%)
8.64	7.50	.138	.0514	
8.64	11.22	.163	.0498	
		Temp., 52°C.		
8.64	5.62	.268	.113	
8.64	7.50	.300	.101	
8.64	7.50	.300	.101	0.104 (±4%)
8.64	11.22	.341	.102	
		Temp., 60°C.		
2.48	2.29	.268	.175	
4.98	2.29	.230	.157	
9.91	2.29	.244	.162	
2.48	4.58	.380	.177	0.169 (±6%)
4.98	4.58	.342	.160	
4.98	4.58	.342	.160	
9.91	4.58	.380	.177	
4.98	9.16	.563	.185	
		Temp., 68°C.		
11.43	5.62	.714	.301	
11.43	7.50	.795	.291	0.311 (±7%)
7.38	7.50	.936	.342	

[a] The concentrations of monomer and catalyst are expressed in g./100 cc. [b] Joseph Dec, Thesis, Doctor of Philosophy, University of Illinois, June, 1940.

Two measurements of the rate of polymerization in the absence of benzoyl peroxide gave good first-order rate constants, although the reaction was more than fivefold slower than the slowest of those carried out in the presence of catalyst. Since no particular precautions were taken to exclude air, there is the possibility that oxygen (or a peroxide resulting from the action of oxygen) may have served as a catalyst for these reactions.

From the values for the rate constants at the different temperatures, the over-all activation energy for the reaction, determined graphically, was found to be 15,200 ± 400 cal.

Conclusions.—In terms of a mechanism for the polymerization, the most plausible explanation for the observed kinetics is a sequence of reactions involving (A) a first-order chain initiating decomposition of the catalyst, (B) a second-order chain-propagating reaction of monomer with an active (free radical) chain generated by (A), and (C) a second-order chain-stopping reaction of two active free radicals.

The most logical course for the chain-initiating process (A) is the first-order decomposition of benzoyl peroxide to generate free radicals.

$$(C_6H_5CO_2)_2 \longrightarrow 2C_6H_5CO_2 \cdot$$
$$C_6H_5CO_2 \cdot \longrightarrow CO_2 + C_6H_5 \cdot \qquad (A)$$
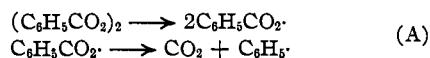
Hey and Waters[6] have presented excellent evidence for such a dissociation of acyl peroxides, based principally on the nature of the products formed by mild thermal decomposition of solutions of various aromatic acyl peroxides. This mechanism is supported further by the plausible explanation it offers for many of the catalytic effects of organic peroxides.[7]

The unimolecular nature of this type of decomposition of acyl peroxides is indicated strongly by measurements of the rate of decomposition of benzoyl peroxide in benzene solution at 80°.[8] Although the values for the first-order rate constants decreased by some 15% during the first half of the reaction, the close agreement between these constants at different initial peroxide concentrations offers convincing support for the first-order kinetics of the thermal decomposition of benzoyl peroxide.
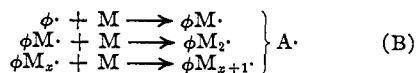
The free radicals formed by decomposition of

the catalyst could then add to the monomer, initiating a free-radical chain reaction leading to the formation of the polymeric substance.[9] Such a mechanism for the growth of polymeric chains has been suggested frequently.[9a]

$$\left. \begin{array}{l} \phi \cdot + M \longrightarrow \phi M \cdot \\ \phi M \cdot + M \longrightarrow \phi M_2 \cdot \\ \phi M_x \cdot + M \longrightarrow \phi M_{x+1} \cdot \end{array} \right\} A \cdot \qquad (B)$$

Neglecting wall reactions or the effect of contaminating inhibitors, the destruction of the free-radical activity of the active chains (A·) involved in the polymerization can be accomplished only through a bimolecular reaction of two of the radicals, either by coupling or by disproportionation

$$2A \cdot \longrightarrow AA \qquad (C)$$
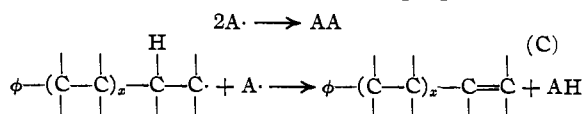
On the basis of this mechanism, the rate of disappearance of the monomer can be expressed as

$$-d[M]/dt = k_B[A \cdot][M] \qquad (3)$$

At the steady state, the rate of formation of free radicals

$$(d[A \cdot]/dt = k_A[Cat])$$

will equal the rate of their destruction

$$(-d[A \cdot]/dt = k_C[A \cdot]^2)$$

The concentration of active chains will thus be proportional to the square root of the catalyst concentration[10]

$$k_A[Cat] = k_C[A \cdot]^2$$

or

$$[A \cdot] = (k_A/k_C)^{1/2}[Cat]^{1/2}$$

and substitution in equation (3) leads to equation (1), the experimentally observed expression for the kinetics of the polymerization.

Summary

An investigation of the kinetics of the benzoyl peroxide-catalyzed polymerization of d-s-butyl α-chloroacrylate in dilute dioxane solution has shown the rate of the reaction to be accurately proportional to the monomer concentration and to the square root of the catalyst concentration.

(6) Hey and Waters, Chem. Rev., 21, 169 (1937).

(7) (a) Kharasch, Mansfield and Mayo, THIS JOURNAL, 59, 1155 (1937); (b) Kharasch and H. C. Brown, ibid., 61, 2142 (1939); 62, 925 (1940); (c) Kharasch, Kane and H. C. Brown, ibid., 63, 526 (1941); see also, e. g., Böeseken and Gelissen, Rec. trav. chim., 43, 869 (1925).

(8) D. J. Brown, THIS JOURNAL, 62, 2657 (1940).

(9) Since the preparation of this manuscript, the suggestion by Kamenskaya and Medvedev [Acta Physicochim. U. R. S. S., 13, 565 (1940)] that chain-initiation may take place through decomposition of the peroxide to generate free radicals has come to the authors' notice.

(9a) See, e. g., Staudinger, Trans. Farad. Soc., 32, 97 (1936); Flory, THIS JOURNAL, 59, 241 (1937); Schulz, Dinglinger and Husemann, Z. physik. Chem., B43, 385 (1939); Melville, Proc. Roy. Soc. (London), A163, 511 (1937); Trans. Inst. Rubber Ind., 15, 209 (1939).

(10) Schulz and Husemann, Z. physik. Chem., B36, 184 (1937); Breitenbach, Monatsh., 71, 275 (1938).

The results are in agreement with the generally accepted mechanism for macropolymerization involving a free radical chain reaction. It has been suggested that, for polymerizations catalyzed by

benzoyl peroxide, the chain is initiated by free radicals formed by thermal decomposition of the catalyst.

The Influence and Behavior of Thiophene on Aromatization Catalysts

BY RICHARD W. HUMMER AND HUGH S. TAYLOR

In view of the present interest in the cyclization and aromatization of petroleum hydrocarbons by catalytic means, it was considered important to investigate the influence of sulfur on this process. We record an investigation on two typical aromatization catalysts, chromium oxide and molybdenum oxide.

These substances were of especial interest since they have been shown to be active in removing sulfur compounds from gasoline and benzene. Orlov and Broun[1] investigated the removal of thiophene from gasoline by hydrogenation at 400° on catalysts of (1) molybdenum trioxide, (2) nickel, cobalt, aluminum and magnesium oxides in the proportions: 42:3:5:1, and (3) cobalt oxide, which were reduced in hydrogen before use. They found the nickel catalyst to be best, but in the light of the investigations of Elgin, Wilder and Taylor[2] (vide infra), they were apparently reporting on the activity before reaching the steady state, since they note that the catalyst rapidly lost activity and could not be regenerated.

Pease and Keighton[3] investigated the efficiency of the removal of thiophene from benzene by hydrogenation. They found an equimolar mixture of cobalt sulfide–molybdenum oxide to be the most efficient. Further investigations by Pease and Munro[4] showed that a cobalt sulfide–chromium oxide catalyst was as efficient as Keighton's best and that a chromium oxide gel although inactive at 200° gave complete removal at 400°.

I. G. Farbenindustrie A.-G. has patented a process for the desulfurization of crude oils by treatment with hydrogen at 300° and ten atmospheres pressure on a molybdenum oxide–zinc oxide catalyst.

Moldavskii and co-workers[5,6] have studied molybdenum sulfide. They showed that at 450° benzene is not hydrogenated whereas thiophene is attacked. At 350°, 90% of the thiophene was already decomposed. They gave the mechanism: thiophene → thiophane → butyl mercaptan. The average velocity of hydrogenation and decomposition of thiophene was also investigated on the sulfides of cobalt, nickel, manganese, cadmium and copper.

In the present investigation, thiophene was chosen since it has been shown to be among the most difficult of such compounds to remove either catalytically or by the usual liquid phase treatments. Elgin,[7] in a study of catalytic action on pure sulfur compounds in a naphtha carrier, found that, at the steady state, the ease of removal was in the order: mercaptan > alkyl sulfide > thiophene. The last was not removed at all after the initial poisoning of the catalyst unless hydrogen was added to the input gases. Faragher, Morrell and Comay[8] found that solutions of thiophene showed no cracking at temperatures up to 870°. Other sulfur compounds, such as sulfides and disulfides, gave hydrogen sulfide, mercaptans, thiophene and elementary sulfur. Malisof and Marks[9] investigated the further cracking of mercaptans and showed that they yield olefins and hydrogen sulfide. For example, butyl mercaptan gave butylene and hydrogen sulfide. This latter reaction is reversible and at lower temperatures, especially in the presence of catalysts, mercaptans can be obtained from olefins plus hydrogen sulfide.[10]

(1) Orlov and Broun, Khim. Tverdogo Topliva, 3, 817–824 (1932).

(2) Elgin, Wilder and Taylor, Ind. Eng. Chem., 22, 1284 (1930); Elgin, ibid., 22, 1290 (1930).

(3) Pease and Keighton, ibid., 25, 1012 (1933).

(4) Pease and Munro, ibid., 25, 1013 (1933).

(5) Moldavskii and Prokopchuk, J. Applied Chem. (U. S. S. R.) 5, 619 (1932).

(6) Moldavskii and Kumari, J. Gen. Chem. (U. S. S. R.), 4, 298–306 (1934).

(7) Elgin, Ind. Eng. Chem., 22, 1290 (1930).

(8) Faragher, Morrell and Comay, ibid., 20, 527 (1928).

(9) Malisof and Marks, ibid., 23, 1114 (1931); 35, 780 (1933).

(10) Sachanen, "Conversion of Petroleum," Reinhold Publishing Co., New York, N. Y., 1940, p. 97.