Photochemical Behavior of O-Ethyl S-Benzyl Xanthate as a Model Compound for a Photosensitive Resin[1]

MAKOTO OKAWARA,[2] TAKESHI NAKAI, YOSHIO OTSUJI, AND EIJI IMOTO

Department of Applied Chemistry, University of Osaka Prefecture, Sakai, Osaka, Japan

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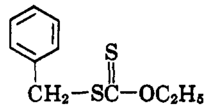
The spectral changes and photoproducts which are produced on photolysis of O-ethyl S-benzyl xanthate (BX) and the photopolymerization of vinyl monomers in the presence of BX are described. The photochemical decomposition of BX, which involves homolytic scission of the S—C(=S) bond *via* an intermediate, gives rise to benzyl mercaptan and carbonyl sulfide, thus serving as an efficient initiating process for polymerization. The chain-transfer constants for BX on photopolymerization are 7.5 for methyl methacrylate and 20.4 for styrene, resulting in 6.2 for Q_{tr} and +0.7 for e_{tr}. The mechanisms of the chain-transfer reaction are discussed.

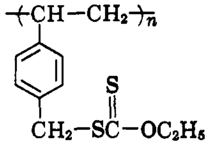
We have previously reported[3] that the polymers containing the N,N-diethyldithiocarbamate group are very effective as photosensitive resins, and that benzyl diethyldithiocarbamate and carbo-*iso*-propoxymethyl diethyldithiocarbamate, the model compounds for these resins, are excellent photosensitizers as well as powerful transfer agents for the polymerization of methyl methacrylate (MMA).

We have, furthermore, found[4] that some xanthates structurally similar to the dithiocarbamate are also photosensitizers for the polymerization of vinyl monomers.

The present work has been initiated in the hope of shedding further light on the photosensitivities of xanthates, and this paper describes the photochemical behavior of O-ethyl S-benzyl xanthate (BX), which is the model compound for the photosensitive polymer (PBX),[4] and the photopolymerization of vinyl monomers in the presence of BX.



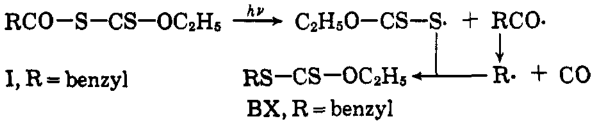
BX



PBX

Results and Discussion

Photolysis of O-Ethyl S-Benzyl Xanthate (BX).—Little information is available on the photolysis of xanthates. Nace and co-workers[5] have suggested the formation of methyl mercaptan during irradiation of (−)-menthyl methyl xanthate from its odor. Barton, George, and Tomoeda[6] have reported that irradiation of O-ethyl S-phenylacetyl xanthate (I) in benzene under reflux gives BX in high yield, and that BX is stable to 8-hr. exposure in Pyrex equipment. They were not interested in looking for further photolysis of xanthate using silica ware. The reaction has been interpreted on the basis of the free-radical mechanism as shown below.



A. Spectral Behavior.—We found that the absorption spectra of BX varied markedly with irradiation in a 1.0-cm. silica cell at a distance of 10 cm. from a high-pressure mercury arc (100 w.). The variations of the recorded spectra with irradiation in ethanol and *n*-hexane are shown in Figures 1 and 2. As can be seen in Figures 1a and 2, an absorption band at about 280 mμ for BX disappeared during irradiation, while a new band appeared in the 240–250-mμ region. The new band gradually disappeared on prolonged irradiation and after 1 hr. no absorption bands appeared in the ultraviolet region. The absorption bands in the 240–250-mμ region reached their maximum values after irradiation for 10 min., independently of the solvents used.

These observations would imply that the species, BX′, whose spectrum has a peak at 243.5 mμ (in ethanol), intervenes as an intermediate for the reaction being studied. The small differences in the pattern of the bands in the 240–250-mμ region in ethanol and *n*-hexane are considered to be due to the solvent effect on the absorption spectra for the intermediate. No attempt was made to isolate the intermediate, but it was proved not to be benzyl mercaptan and carbonyl sulfide, which were isolated as photolytic products (see later section). The depression of the absorbance for the degassed solution compared with an aerated one seems to be due to the smaller contributions of the process, BX → BX′, for the former.

In addition we observed that the infrared spectra varied when a carbon tetrachloride solution of BX was irradiated in a closed sodium chloride cell (0.1 mm.) by means of a high-pressure mercury arc. Figure 3 shows the recorded infrared spectra at various time intervals. Under irradiation a sharp band gradually appeared at 2040 cm.$^{-1}$. The new band was assigned to the asymmetric stretching vibration of carbonyl sulfide and this was confirmed by comparison with the infrared spectrum of the authentic compound isolated from the pyrolysis of BX. Other bands remained unchanged with irradiation.

B. Isolation of the Photoproducts.—From the preliminary experiments described above, BX was found to decompose on exposure to light. The isolation of the main photoproducts using the apparatus described in the previous paper[3] was attempted. A solution of

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[1] Part XIX in a series on the syntheses and reactions of functional polymers. Part of this paper was presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1964.

[2] To whom correspondence should be addressed at the Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Meguro, Tokyo, Japan.

[3] Part XVI: M. Okawara, H. Yamashina, K. Ishiyama, and E. Imoto, *Kogyo Kagaku Zasshi*, **66**, 1383 (1963).

[4] M. Okawara, T. Nakai, and E. Imoto, *ibid.*, in press.

[5] H. R. Nace, D. G. Manly, and S. Fusco, *J. Org. Chem.*, **23**, 687 (1958).

[6] D. H. R. Barton, M. V. George, and M. Tomoeda, *J. Chem. Soc.*, 1967 (1962).

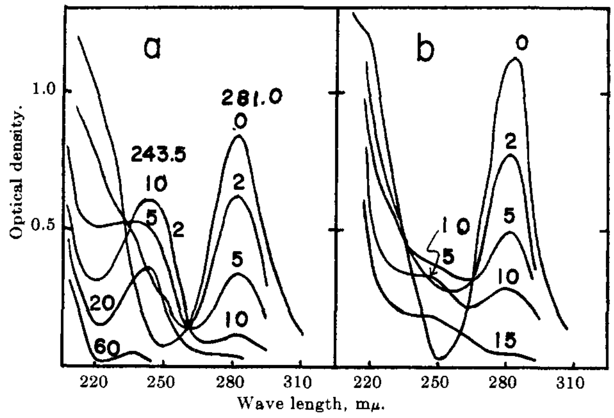


Figure 1.—Ultraviolet spectral changes of O-ethyl S-benzyl xanthate (BX) with irradiation in air-saturated (1a) and degassed (1b) ethanol solution; $[BX]_{air\text{-}satd} = 6.59 \times 10^{-5}$, $[BX]_{degassed} = 8.71 \times 10^{-5}$ mole/l. Numbers denote the time of irradiation (minutes).

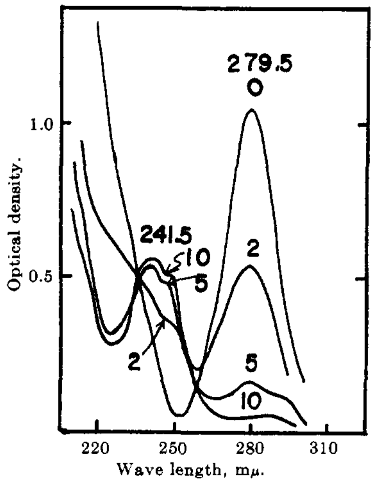


Figure 2.—Ultraviolet spectral changes of O-ethyl S-benzyl xanthate (BX) with irradiation in air-saturated *n*-hexane solution; $[BX] = 8.11 \times 10^{-5}$ mole/l. Numbers denote the time of irradiation (minutes).

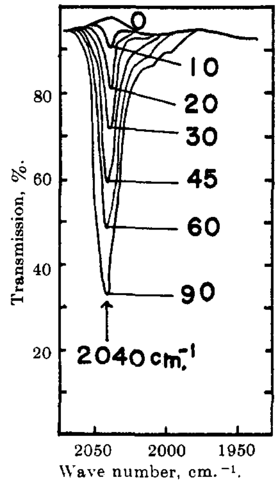
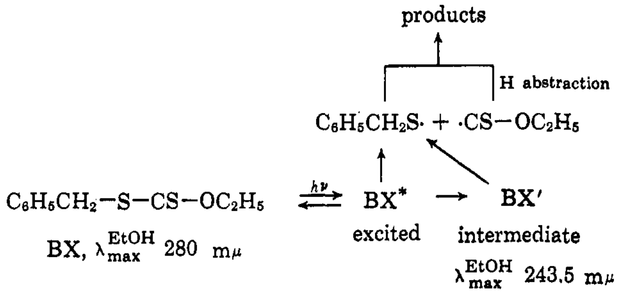


Figure 3.—Infrared spectral changes of O-ethyl S-benzyl xanthate (BX) with irradiation in a carbon tetrachloride solution; $[BX] = 0.25$ mole/l., at 23°. Numbers denote the time of irradiation (minutes).

BX in benzene was irradiated by means of a high-pressure mercury arc at room temperature for 15 hr. in a nitrogen atmosphere. Careful distillation of the irradiated solution gave a small fraction which had the odor of mercaptan. The reaction of this fraction with 3,5-dinitrobenzoyl chloride produced S-benzyl 3,5-dinitrothiobenzoate. The other fractions were shown from their ultraviolet spectra to be unchanged BX. The yield of the benzoate was not affected by changing the solvent from benzene (aprotic) to 95% ethanol (protonic).

These results indicate that the photolysis of BX gives benzyl mercaptan and carbonyl sulfide as the main products although the yields are very low.[7]

C. **Mechanism.**—The formation of the mercaptan must be explained on the basis of intramolecular hydrogen abstraction, since solvent effects were not observed either on the rate of the reaction measured from ultraviolet spectral changes or from the yield of the mercaptan. The photolysis of BX must also proceed through the free-radical mechanism, which conclusion is supported from the results of photopolymerization (see later section). These considerations led us to suppose the following scheme for the photolysis of BX.



It is interesting to note that the mechanism proposed here is not in agreement with the Chugaev reaction for the pyrolysis of xanthates. In the case of the pyrolysis,[8] the reaction proceeds through the molecular (nonradical) mechanism accompanied by intramolecular hydrogen abstraction and the formation of ethylene.

Photopolymerization of Styrene and Methyl Methacrylate (MMA).—An example of photopolymerization using xanthates as the sensitizer can be found only in a patent,[9] which does not refer to the reaction mechanism. Figure 4 shows some examples of the time–conversion curves for the bulk polymerization of styrene and MMA in the presence of BX. Since the time–conversion curves were straight lines, the rate of polymerization, R_p, was determined from their slopes. When the R_p values were plotted against the square root of the concentrations of the photosensitizer, a linear relationship was obtained as shown in Figure 5. The dependence of BX concentrations on the rates of polymerization of styrene and MMA agrees with "the square-root rule."

From measurements of the radioactivities of polymers obtained from photopolymerization in the presence of the radioactive BX, O-ethyl S-benzyl-α-C^{14} xanthate (BX_a), the average content of C^{14} in the polymers was found to be 1.1 and 1.7 atoms/macromolecule for polystyrene and poly(methyl methacrylate), respectively, as shown in Table I. When the radioactivities

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[7] It is interesting to note that the bond rupture due to the photolysis occurs at S—C(=S) for BX and at CH₂—S for benzyl diethyldithiocarbamate.[3]

[8] H. R. Nace, *Org. Reactions*, **12**, 57 (1962).

[9] V. A. Englehardt and M. L. Peterson, U. S. Patent 2,716,633 (1955); *Chem. Abstr.*, **50**, 1365 (1956).

TABLE I

RESULTS OF RADIOACTIVITY MEASUREMENTS ON POLY(METHYL METHACRYLATE) (PMMA) AND POLYSTYRENE (PSt)

Polymer	Concn. of BX_a: $M \times 10^3$	Concn. of BX_a: $\bar{M}_n$[a] $\times 10^{-5}$	Radioactivity[b]: C.p.m./g. of polymer $\times 10^{-4}$	Radioactivity[b]: C.p.m./macromolecule $\times 10^{-9}$	Average content, atoms/macromolecule
PMMA	0.14	2.84	0.870	2.49	1.60
	1.07	1.63	1.033	1.68	1.08
	1.60	1.34	1.730	2.32	1.49
	2.13	1.26	2.131	2.68	1.72
	5.13	1.08	2.457	2.65	1.70
	7.70	1.02	2.863	2.81	1.80
PSt	1.11	0.172	9.629	1.66	1.06
	1.11		9.374	1.62[c]	1.04
	1.73	0.135	11.08	1.50	0.98
	1.73		12.18	1.64[c]	1.05

[a] The number-average molecular weight calculated viscometrically. [b] Measurements were made with polymers obtained after 90 min. of irradiation. [c] Calculated from the radioactivity of the polymer obtained after 140 min. of irradiation, assuming that the molecular weight of the polymer was equal to that of the polymer after 90 min.

for 1 g. of polymer were plotted against the concentrations of BX_a, the linear relationship shown in Figure 6 was obtained.

Furthermore, in our paper,[4] we found that the rates of photopolymerization of vinyl monomers were almost proportional to the square roots of the rates of photodecomposition of xanthates when $C_6H_5(CH_2)_n$–SCS–OC_2H_5 (n = 0, 1, or 2) was used as an initiator.

These facts indicate that the photopolymerization is not initiated by transfer of electronic excitation energy from excited BX to a monomer molecule, but by means of the free-radical mechanism. In this case, the xanthate BX is decomposed photochemically into free radicals to initiate the polymerization.

The Chain-Transfer Reaction.—In this investigation, chain-transfer constants were determined by the following two methods, based on the photopolymerization data of styrene and MMA.

Firstly, transfer constants were calculated from eq. 1 according to Mayo,[10] where C_s is a chain-transfer

$$1/\bar{P}_n = 1/\bar{P}_0 + C_s[S]/[M] \qquad (1)$$

constant of the sensitizer BX, $\bar{P}_0$ and $\bar{P}_n$ are the degrees of polymerization in the absence and presence of BX, respectively, and [S]/[M] is the average molar ratio of BX to monomer. In Figure 7 $1/\bar{P}_n$ is plotted against [S]/[M]. Both for MMA and styrene, these plots gave straight lines. The chain-transfer constants (*i.e.*, the slopes of those lines) are 2.5 and 25 for MMA and styrene, respectively.

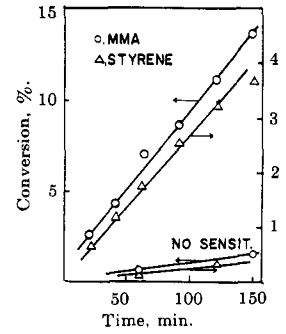

Figure 4.—Examples of time–conversion curves on photopolymerization of MMA and styrene.

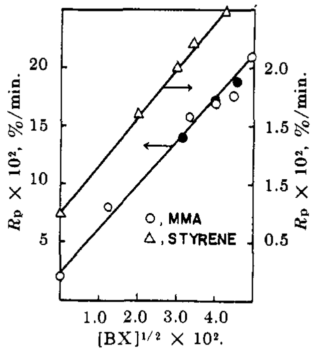

Figure 5.—Variations in polymerization rate with the initial concentration of O-ethyl S-benzyl xanthate (BX) for MMA and styrene.

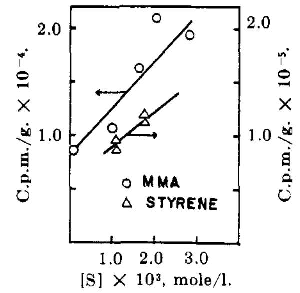

Figure 6.—Plots of the radioactivity of polymer *vs.* the initial concentration of O-ethyl S-benzyl-α-C^{14} xanthate (BX_a).

Secondly, transfer constants were calculated from eq. 2 according to Walling,[11] where R is the ratio of measured radioactivities of polymers from two experiments, [S] is concentration of BX_a present initially (subscript zero) and at the end of the two experiments (subscripts one and two), and $[M]_1$ and $[M]_2$ are monomer concentrations calculated from conversions after 90 and 140 min., respectively.

$$R\frac{1 - [M]_1/[M]_0}{1 - [M]_2/[M]_0} = \frac{1 - ([M]_1/[M]_0)^{C_s}}{1 - ([M]_2/[M]_0)^{C_s}} \qquad (2)$$

$$R = \frac{[S]_0 - [S]_1}{[M]_0 - [M]_1} \bigg/ \frac{[S]_0 - [S]_2}{[M]_0 - [M]_2} \qquad (3)$$

Since R is measurable, C_s can be determined from eq. 2. Equation 2 holds only in the case that all polymer radicals terminate by chain transfer.[11] The chain-transfer constants obtained are shown in Table II to-

TABLE II

DETERMINATION OF C_s VALUE ON PHOTOPOLYMERIZATION OF MMA AND STYRENE BY EQUATION 2

Monomer	Concn. of BXa, $M \times 10^3$	$[M]_1/[M]_0$	$[M]_2/[M]_0$	Radioactivity, c.p.m./g. $\times 10^{-4}$: Expt. 1[a]	Radioactivity, c.p.m./g. $\times 10^{-4}$: Expt. 2[b]	R	C_s
MMA	1.60	0.874	0.780	1.730	1.316	1.314	7.50
	2.13	0.869	0.771	2.131	1.357	1.570	10.7
Styrene	1.11	0.980	0.976	9.629	9.374	1.027	15.0
	1.73	0.978	0.968	12.181	11.083	1.099	20.4

[a] Radioactivity of polymer obtained after 90 min. of irradiation. [b] Radioactivity of polymer obtained after 140 min. of irradiation.

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(10) F. R. Mayo, R. A. Gregg, and W. S. Mathieson, *J. Am. Chem. Soc.*, **73**, 1691 (1951). Equation 1 required that [S]/[M] remain constant during polymerization. Therefore, for most chain-transfer agents with a large C_s value, an accurate value cannot be obtained from this equation.

(11) C. Walling, *ibid.*, **70**, 2561 (1948).

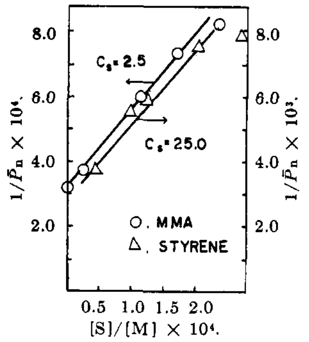

Figure 7.—Determination of chain-transfer constants for MMA and styrene *via* eq. 1.

gether with the measured data. The chief interest of these data on chain-transfer constants lies in the fact that their values calculated from eq. 1 are of the same order of magnitude as those calculated from eq. 2 and that the values for styrene are much larger than those for MMA. The former fact shows that the termination predominantly occurs through a transfer reaction and that only polymer radicals induced the decomposition of BX. The latter fact indicates that BX is an electron-withdrawing transfer agent. The C_s values for BX on photopolymerization are extraordinarily large as compared with those of related compounds. For example, the C_s value of dibenzyl disulfide is 0.03 for styrene, in which the chain-transfer reaction proceeds by means of the attack by the polymer radical on both the benzyl hydrogen and disulfide sulfur atoms.[12] The transfer constant for BX is rather close to that for benzyl mercaptan (25 for styrene),[13] in which the chain-transfer reaction proceeds by means of mercapto-hydrogen abstraction. In the present case, in which such a labile hydrogen is lacking, the large C_s value for BX may be due to the partial rupture or releasing of the S—C(=S) bond in the photoexcited transition state of the transfer reaction.

For the chain-transfer reaction, two probable schemes (4 and 7) may be expected where Mn· is a radical

$$\left\{\begin{array}{ll} \mathrm{Mn\cdot} + \mathrm{BX^*} \longrightarrow \mathrm{Mn{-}SCH_2C_6H_5} + \mathrm{\cdot CS{-}OC_2H_5} & (4) \\ \mathrm{C_2H_5O{-}CS\cdot} + \mathrm{M} \longrightarrow \mathrm{C_2H_5O{-}CS{-}M\cdot} \longrightarrow & (5) \\ \mathrm{C_2H_5O{-}CS\cdot} \longrightarrow \mathrm{COS} + \mathrm{C_2H_5\cdot} \longrightarrow \mathrm{C_2H_5{-}M\cdot} \longrightarrow & (6) \end{array}\right.$$

$$\mathrm{Mn\cdot} + \mathrm{BX^*} \longrightarrow \mathrm{Mn{-}CS{-}OC_2H_5} + \mathrm{C_6H_5CH_2{-}S\cdot} \qquad (7)$$

of a growing chain and BX* is a molecule of BX in the excited state.

If the transfer reaction occurs *via* reaction 4, the average content of C^{14} will be over 1 atom/macromolecule. If reaction 7 predominates, the content will be below one atom. Since the average contents measured were over 1 atom/macromolecule for both polystyrene and poly(methyl methacrylate), the actual transfer process involved should be reaction 4, followed by the initiation reaction 5 or 6.

Furthermore, the Q_{tr} and e_{tr} values for BX were calculated according to the Mesrobian method[14] using a Q–e scheme for copolymerization data. The values obtained were 6.2 for Q_{tr} and +0.7 for e_{tr}. This shows that BX facilitates the chain-transfer reaction when the end of a growing chain radical is negatively charged. Although a reasonable explanation for the extremely large Q_{tr} value can not be attained in this stage, it may be supposed that the electronically excited BX molecule plays some role in the resonance stabilization of the transition state for the reaction. Okamura, *et al.*,[15] have pointed out that the Q_{tr} values for various aromatic hydrocarbons increase in parallel with the extent of radical stabilization at the transition state in the transfer reaction.

Experimental[16]

Preparation of O-Ethyl S-Benzyl Xanthate (BX).—In accordance with the method of Djerassi, *et al.*,[17] 13 g. of benzyl chloride was added dropwise to a solution of 16 g. of potassium ethyl xanthate in 60 ml. of acetone, the temperature being kept below 30°. The mixture was refluxed for 3 hr. on a steam bath. After cooling to room temperature, the mixture was poured into water, the product was extracted with ether, the extract was dried over sodium sulfate, and the solvent was removed *in vacuo*. The residue was distilled under reduced pressure and 17.5 g. (88.5%) of crude product (b.p. 148–156° at 9 mm.) was obtained. The crude product was purified by redistillation, b.p. 154–156° at 9 mm., $n^{16.5}\mathrm{D}$ 1.6059 (lit.[16] b.p. 145–147° at 4 mm., $n^{30}\mathrm{D}$ 1.5952).

Preparation of O-Ethyl S-Benzyl-α-C^{14} Xanthate (BX_a).—Benzyl-α-C^{14} chloride was prepared in the manner reported by Bergel, *et al.*,[18] starting with phenylmagnesium bromide and carbon dioxide evolved from barium carbonate-C^{14}. By reaction of benzyl-α-C^{14} chloride with potassium ethyl xanthate, the labeled xanthate BX_a was obtained. The radioactivity of BX_a was 7.364×10^6 c.p.m./g. (1.561×10^9 c.p.m./mole).

Isolation of the Photoproducts.—The isolation of the main photoproducts was performed by means of the internal irradiation reported previously.[3] A solution of 5 g. of BX in 350 ml. of thiophene-free, dry benzene was placed in the reaction vessel. The solution was irradiated with a high-pressure mercury lamp (100 w.) at room temperature for 15 hr. in a nitrogen atmosphere. After the irradiation was stopped, the solvent was removed *in vacuo* in a nitrogen atmosphere and the residue was distilled under reduced pressure. A small amount (*ca.* 100 mg.) of the first fraction (b.p. <130° at 10 mm.), which had the odor of mercaptan and decolorized an iodine solution, was obtained. Reaction of this fraction with 3,5-dinitrobenzoyl chloride produced a solid which was recrystallized from ethanol to give white needles with m.p. 118–119°. This benzoate was identified as S-benzyl 3,5-dinitrothiobenzoate (lit.[19] m.p. 119–120°) from the mixture melting point and by agreement of the infrared spectra with that of the authentic material. The other fractions were proved to be unchanged BX from their boiling points and ultraviolet spectra.

Polymerization Procedure.—All polymerizations were carried out in bulk. Purified monomer was added to a given amount of the sensitizer in a hard-glass tube. The tube was then degassed under vacuum by the usual freezing and thawing technique and then sealed. The tubes were fixed on a rotating wheel (33 cycles/min.) and irradiated by a Matsuda SHL-type high-pressure mercury lamp placed at the center of the circle. The reaction temperature was maintained at 22 ± 2° during irradiation. After a given interval the tube was removed from the wheel and

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(12) R. M. Pierson, A. J. Contanza, and A. H. Weinstein, *J. Polymer Sci.*, **17**, 221 (1955).

(13) V. A. Dinaburg and A. A. Vanskeidt, *J. Gen. Chem. USSR*, **24**, 839 (1954).

(14) N. Fuhrman and R. B. Mesrobian, *J. Am. Chem. Soc.*, **76**, 3281 (1954). Chain-transfer data have been applied to the Alfrey–Price Q–e scheme, that is the relationship, $C_s = Q_{tr}/Q_1 e^{-e_1(e_{tr}-e_1)}$, where Q_{tr} and Q_1 are general reactivities, and e_{tr} and e_1 are polar constants of a chain-transfer agent and monomer, respectively.

(15) K. Katagiri, K. Uno, and S. Okamura, *J. Polymer Sci.*, **17**, 142 (1955).

(16) Infrared spectra were obtained with a Hitachi EPI-2 infrared spectrophotometer with sodium chloride cells. Ultraviolet spectra were measured using 1-cm. silica cells, with a Hitachi EPS-2 recording spectrometer.

(17) C. Djerassi, M. Gorman, F. X. Markley, and E. B. Oldenburg, *J. Am. Chem. Soc.*, **77**, 568 (1955).

(18) F. Bergel, V. C. E. Burnop, and J. A. Stock, *J. Chem. Soc.*, 1223 (1955).

(19) E. Wertheim, *J. Am. Chem. Soc.*, **51**, 3662 (1929).

the polymerization product was precipitated by adding methanol. Conversion was calculated from the weight of the polymer obtained in the dry state. Viscosity measurements were made in benzene solution with an Ostwald viscometer at 30°. The number-average degrees of polymerization were calculated from the Tobolsky equation[20] for MMA and from that of Mayo[10,21] for styrene: MMA, $\log \bar{P}_n = 3.420 + 1.13 \log [\eta]$; styrene, $\log \bar{P}_n = 3.204 + 1.37 \log [\eta]$.

Counting Procedure.—Radioactive polymers were purified by triple precipitation (toluene–methanol).[22] Radiocarbon analyses were performed with a Packard Tri-Carb liquid scintillation spectrometer, Model 314-AX, using 20-ml. potassium-free, No-Vit glass, liquid scintillation spectrometer vials with tinfoil-lined, toluene-resistant caps. Packard Instrument Co. scintillation grade 2,5-diphenyloxazole (PPO) and *p*-bis[2-(5-phenyloxazole)]-benzene (POPOP) were used as primary and secondary scintillators, respectively. The scintillation solution consisted of 3.50 g. of PPO and 0.100 g. of POPOP dissolved in 1 l. of Wako reagent grade toluene. A sample was prepared for counting by pipetting 20.0 ml. of scintillation solution into a vial containing a known amount of active polymer.

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(20) B. Baysal and A. V. Tobolsky, *J. Polymer Sci.*, **9**, 171 (1952).

(21) D. C. Pepper [*ibid.*, **7**, 347 (1951)] has verified this relation for low molecular weight polymers.

(22) Difficulties encountered in the purification procedure in such experiments are that fractionation of polymer accompanies the purification. J. Bevington's work [*Proc. Roy. Soc* (London), **A221**, 437, 453 (1954); *J. Polymer. Sci.*, **12**, 449 (1952); **14**, 463 (1954)] and E. M. Arnett's work [*J. Am. Chem. Soc.*, **74**, 2031 (1952)] have given assurance that double precipitations can remove almost all the uncombined initiator.

Kinetics of Iodination. II. General Base Catalysis in the Iodination of N-Acetyl-L-tyrosine and N-Acetyl-3-iodo-L-tyrosine

W. E. MAYBERRY[1] AND D. A. BERTOLI

National Institute of Arthritis and Metabolic Diseases, National Institutes of Health, Bethesda, Maryland

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The effect of buffers over the pH range 5.40 to 9.80 upon the rates of iodination of N-acetyl-L-tyrosine and N-acetyl-3-iodo-L-tyrosine has been studied. Evidence is presented for general base catalysis in both iodination reactions. The effectiveness of the bases as catalysts follows the order $OH^- \gg CO_3^{-2} > HPO_4^{-2} > C_8H_{11}N_2O_3^- > CH_3COO^- > HCO_3^- > H_2PO_4^- \gg H_2O$. The data fit the Brønsted relationship, $k_b = G_b(1/K)^\beta$. The presence of general base catalysis supports the concept of iodination of phenoxide ion by molecular iodine through a quinoid intermediate but does not rule out H_2OI^+ as the iodinating species.

Halogenation reactions were among the reactions associated with the development of the classic theory of general acid–base catalysis.[2] An effect of the buffer constituents has been noted consistently in the iodination of phenol and derivatives of phenol. Painter and Soper[3] felt that their results in the iodination of phenol were compatible with acid catalysis, while Berliner[4] presented kinetic results for the iodination of aniline and phenol in phosphate buffers which were indicative of base catalysis. The iodination of 2,4-dichlorophenol was thought also to be catalyzed by base.[5]

Li[6] has studied the effect of acetate and phosphate buffers upon the rate of iodination of tyrosine. In phosphate buffer it was reported that a plot of the observed rate constant *vs.* dibasic phosphate ion concentration was linear according to the relationship in eq. 1 where k_{OH}, k_{HA}, and k_{H_2A} are catalytic constants reflecting the efficiency of hydroxyl, dibasic phosphate, and monobasic phosphate ions, respectively. K_W is the ion product of water and K_{H_2A} is the equilibrium dissociation constant for eq. 2. Interpretation of Li's data is complicated in that the kinetic results probably reflect both monoiodination and diiodination.

$$k_{obsd} = k_{OH}K_W\frac{1}{[H^+]} + [HPO_4^{-2}]\left(k_{HA} + \frac{k_{H_2A}}{K_{H_2A}}[H^+]\right) \qquad (1)$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{-2} + H^+ \qquad (2)$$

The effect of phosphate buffer components upon the iodination of N-acetyl-L-tyrosine and N-acetyl-3-iodo-L-tyrosine has previously been shown to follow the form of eq. 3,[7] where k_0 represents the "uncatalyzed" or water reaction. Thus, the evidence presented has been suggestive of general base catalysis in phenolic iodination, but conclusive evidence for such has not been formulated. To study this possibility, the effects of buffers upon the kinetics of iodination has been investigated over a wider range of hydrogen ion concentration and with several different buffers. The studies have been facilitated by a high-speed digital computer program, and evidence for general base catalysis is presented.

$$k_{obsd} = k_0 + k_{HA}[HPO_4^{-2}] + k_{H_2A}[H_2PO_4^-] \qquad (3)$$

Experimental

Materials.—The N-acetyl-L-tyrosine and N-acetyl-3-iodo-L-tyrosine[8] were the same preparations as recently reported.[9] The buffer reagents were reagent grade chemicals. Glass-distilled water was used.

Buffer solutions were prepared at a given pH in the highest concentration reported, and volumetric dilutions of this concentration were made to achieve varying concentrations of buffer constituents. Total ionic strength was maintained at 0.64 by the addition of sodium chloride.

The concentration of buffer species was calculated from the appropriate equilibrium dissociation constants at 25° and at infinite dilution for the sodium bicarbonate–sodium carbonate,[10]

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(2) See R. P. Bell, "The Proton in Chemistry," Methuen and Co., Ltd., London, 1959, p. 223 ff, for extensive review and reference.

(3) B. S. Painter and F. G. Soper, *J. Chem. Soc.*, 342 (1947).

(4) E. Berliner, *J. Am. Chem. Soc.*, **72**, 4003 (1950); **73**, 4307 (1951).

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(6) C. H. Li, *ibid.*, **66**, 228 (1944).

(7) W. E. Mayberry and J. E. Rall, *Exposes Ann. Biochim. Med.*, **25**, 21 (1964).

(8) Abbreviations, N-acTY and N-acMIT, will be used for N-acetyl-L-tyrosine and N-acetyl-3-iodo-L-tyrosine, respectively. We are grateful to Dr. Rosalind Pitt-Rivers for generously supplying these compounds.

(9) W. E. Mayberry, J. E. Rall, and D. Bertoli, *J. Am. Chem. Soc.*, **86**, 5302 (1964).

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