tures indicated the presence of 5–10% of III. Recrystallization gave a nearly pure sample of 3-*p*-tolylsulfonyl-1-cyclohexene, m.p. 59–61°.[11a]

Attempts at Purification of Xanthates.—Freshly prepared xanthates of the sulfone and sulfide alcohols I, II, V and VI all resisted attempts at crystallization and purification. Working with *trans*-2-*p*-tolylsulfonylcyclohexanol as a model, several attempts at purification of the resulting xanthate were made. Important observations include (1) removal of the solvent from the reaction mixture using a steam-bath gave some decomposition to olefin; (2) attempted distillation of the xanthate gave complete decomposition to olefin at low pressures (0.2 mm.); (3) chromatography over activated silica failed to separate a small amount of alcohol from the xanthate.

To evaluate the relative amounts of xanthate present in the crude reaction products a simple distillation flask connected to three cold traps for collecting and weighing carbon oxysulfide and methyl mercaptan was set up. Decompositions were carried out in a nitrogen atmosphere. Using cholesterol xanthate, m.p. 125–128° (reported[8] m.p. 127.5–128°), 102–104 weight per cent. of the theoretical quantity of volatile decomposition products was observed. The xanthates of I and II on similar treatment gave 81 and 78 weight per cent. of theoretical carbon oxysulfide and methyl mercaptan, reflecting relative purities of about 80%.

Kinetics.—Relative reaction rates were determined by loss of weight for a specific xanthate in tared erlenmeyers immersed in an oil-bath maintained at 166 ± 2°. After a specific time interval at the indicated temperature the reaction flasks were quenched in cold benzene and reweighed. Comparative rates are then expressed in terms of percentage unreacted xanthate at specific time intervals. This is essentially the procedure of O'Conner and Nace.[8] Approximate first-order rate constants were obtained by plotting the logarithm of percentage unreacted xanthate against the time in minutes. The rate constant k is equal to $-2.303 \times$ slope of the line of this plot. The approximate first-order rate constant obtained in this way for *trans*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate was 10.2×10^{-3} min.$^{-1}$. For the *cis* analog the rate constant was 4.37×10^{-3} min.$^{-1}$.

Ultraviolet Absorption Measurements.—Ultraviolet absorption spectra of the α,β- and β,γ-unsaturated sulfones III and IV and mixtures of these two isomers were determined using a Beckman DK-2 recording spectrophotometer. Concentrations of 4×10^{-5} *M* compound in 95% ethanol gave convenient (60%) transmittance. The absorption maxima for the sulfones are 235 mμ for pure III and 226 for pure IV. The maxima for synthetic mixtures were: 234 for 90% III + 10% IV; 232 for 80% III + 20% IV; 230 for 60% III + 40% IV; 227 for 10% III + 90% IV.

Tests for Rearrangement. (1) **During Pyrolysis.**—Two and eight-tenths grams of 3-*p*-tolylsulfonyl-1-cyclohexene (IV) and 8.5 g. (0.0247 mole) of *trans*-2-*p*-tolylsulfonylcyclohexyl S-methyl xanthate were mixed and placed in a 25-ml. distillation flask. The flask contents were heated under nitrogen for ten minutes at 220°, vacuum was applied and the product distilled slowly under 2 mm. vacuum. Seven and six-tenths grams of an oil, which slowly crystallized, was collected. The crude solid, 4×10^{-5} *M* in 95% ethanol, gave maximum ultraviolet absorption at 230 mμ indicating about 60% 1-olefin III and 40% 3-olefin IV. The product should contain about 65% III and 35% IV if no rearrangement occurs.

Refluxing 105 mg. (0.42 millimole) of IV with 80 mg. (0.42 millimole) of *p*-toluenesulfonic acid in 10 ml. of 1-octanol (b.p. 194–195°) also failed to cause rearrangement as measured by ultraviolet absorption. Refluxing 0.1 g. of potassium in 30 ml. of *t*-butyl alcohol with 1.05 g. of III for six hours caused rearrangement to the extent of about 20%; the amount of IV did not increase appreciably during another 16-hour reflux period with potassium *t*-butoxide in *t*-butyl alcohol. Under similar conditions 1.0 g. of IV and 0.1 g. of potassium in 30 ml. of *t*-butyl alcohol caused slow rearrangement to III, 50% rearrangement occurring in 6 hours and a mixture of 25% IV and 75% III was obtained after 22 hours. In all cases the products were isolated from the reaction mixture by the addition of cold water, extraction of the aqueous solution with chloroform, and evaporation of the solvent from the extract leaving the solid residues on which all ultraviolet absorption measurements were made directly.

(2) **Of *cis*-Alcohol During Salt Formation.**—One and six-tenths grams (0.007 mole) of *cis*-2-*p*-tolylsulfonyl-1-cyclohexanol in 20 ml. of dry benzene was stirred with 0.20 g. of metallic potassium for five hours. The benzene was removed under a stream of nitrogen and the mushy solid residue treated with 20 ml. of 5% HCl. The insoluble white solid was removed by filtration and washed with water and 5% HCl. The dried residue gave a m.p. of 85–89° and infrared analysis showed no evidence for formation of the *trans* isomer.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Hydrogen Bromide Cleavage of Hindered 2-Methoxyacetophenones

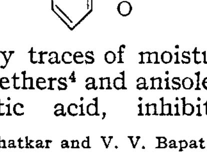
BY W. J. HORTON AND JACK T. SPENCE[1]

RECEIVED SEPTEMBER 9, 1957

The facile cleavage of 3-substituted-2-methoxyacetophenones is ascribed to the steric influence of the 3-substituent. The rate of cleavage of a number of such compounds has been determined and these data as well as ultraviolet spectra support the proposal of steric inhibition of resonance by the 3-substituent.

The room temperature cleavage of 2-alkoxyacetophenones by means of hydrogen bromide-acetic acid was shown previously to be promoted by a methoxy group in the 3-position, whereas a 5-methoxy group lacked this influence.[2] This facile cleavage was first observed in methoxybenzosuberones.[3]

In a kinetic study of the conversion of 2,3-dimethoxyacetophenone (I) to 2-hydroxy-3-methoxyacetophenone by means of hydrogen bromide-acetic acid it has been found that the reaction is first order with respect to I; that the order of the reaction is two and by inference, the reaction is first order with respect to hydrogen bromide. It was found that the rate of the reaction was greatly influenced by traces of moisture. In the cleavage of naphthol ethers[4] and anisole[5] by aqueous hydrohalogen-acetic acid, inhibition by increasing



I, R = OCH_3
II, R = CH_3

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(1) From the Doctoral Dissertation of Jack T. Spence.

(2) (a) W. J. Horton and J. T. Spence, THIS JOURNAL, **77**, 2894 (1955); (b) P. D. Gardner, W. J. Horton and R. E. Pincock, *ibid.*, **78**, 2541 (1956).

(3) P. D. Gardner and W. J. Horton, *J. Org. Chem.*, **19**, 213 (1954).

(4) G. P. Kolhatkar and V. V. Bapat, *J. Univ. Bombay*, **7**, Pt. 3, 157 (1938); *C. A.*, **33**, 5268 (1939).

(5) R. P. Ghaswalla and F. G. Donnan, *J. Chem. Soc.*, 1341 (1936).

amounts of water was noted. The inhibition in the cleavage of diethyl ether by anhydrous hydrogen bromide[6] was avoided by the addition of acetyl bromide.

The decrease in the rate of the reaction of I after *ca.* 60% had reacted is unexplained. A similar deceleration in the cleavage of diethyl ether[6] was shown to be due to the ethanol produced which deprived an equivalent amount of hydrogen bromide of its ability to cleave the ether. The deceleration in the present work was unchanged by the addition of the cleaved compound and was also found in those runs containing a large excess of hydrogen bromide.

Table I contains second-order rate constants for I, II and for 5-bromo- and 5-nitro-2,3-dimethoxyacetophenone. Reliable data could not be obtained for 2-methoxy-, 2,5-dimethoxy- or 2-methoxy-5-methylacetophenone due to side reactions which made analytical measurements difficult. Such data as could be obtained supported the slow cleavage which is to be expected for compounds having no substituent in the 3-position.[2]

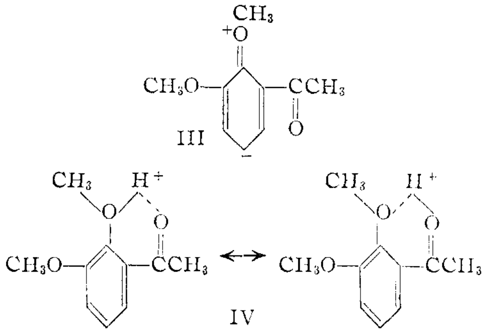
TABLE I

SECOND-ORDER RATE CONSTANTS

Equimolar hydrogen bromide and substituted acetophenone, mole/l.	$k_2 \times 10^3$ at 25.15 ± 0.05°, moles^{-1} min.$^{-1}$
2,3-Dimethoxyacetophenone	
0.274	30.3
.295	32.2
.402	32.3
.536	32.8
2-Methoxy-3-methylacetophenone	
0.147	33.9
.295	35.4
.443	35.7
.590	36.8
2,3-Dimethoxy-5-bromoacetophenone	
0.275	5.68
.442	6.05
.552	5.86
.737	6.36
2,3-Dimethoxy-5-nitroacetophenone	
0.135	1.29
0.268	1.28
1.215[a]	1.33

[a] Ketone was 0.136 mole/l.

The rate constants indicate that the size of the substituent in the 3-position is responsible for the more rapid cleavage of 3-substituted-2-methoxyacetophenones. It should be noted that the cleavage of II demonstrates for the first time that cleavage at room temperature may occur with groups other than methoxy.[2,7a] It is clear from the rate constants that the reaction is adversely influenced by an electrophilic group in the 5-position.[8] These results are in harmony with the proposal that the resonance form III is sterically inhibited by the 3-substituent.[7] Such an inhibition increases the basicity of the oxygen atom at position 2 and promotes the approach of a proton or a dipolar hydrogen bromide molecule. The known reaction products then follow by SN2 attack by a bromide ion or by an SNi reaction. The formation of an oxonium salt similar to IV has been proposed for the selective cleavage of *o*-alkoxyaryl ketones[9] and evidence contraindicative of hydrogen bonding has been presented.[10] Steric inhibition of III would remove the objection to IV based on the positive character of the oxygen atom at position 2.[10] That protonation is not a sufficient condition for cleavage has been shown by the failure of I to cleave in perchloric acid–acetic acid, sulfuric acid–acetic acid or hydrogen chloride–acetic acid.



III

IV

The ultraviolet spectra of I and II give added support to the proposal of suppression of the resonance form III. Analogous to the work of Cram on the additivity of $\Delta m\mu$'s[11] on insertion of a methyl group or groups into 2,4- and 2,6-dihydroxyacetophenones, the $\Delta m\mu$'s for hydroxy, methoxy and methyl groups in acetophenone (Table II) permit the calculation of absorption maxima from the parent compound, acetophenone. The data are summarized in Table II.

The band positions for the individual acetophenones, calculated by summation of the appropriate individual contributions agree with the experimentally determined values except in instances of steric influence. The deviation for steric reasons was noted in methyldihydroxyacetophenones.[11] The order of steric influence may be judged by the lowering of the intensity of the secondary band in corresponding pairs of compounds (2,5- minus the 2,3-compound). This lowering is of a similar order for methyl and methoxyl (relative to hydroxyl) which is also true of the deviations from the calculated secondary bands and true of the rate constants (Table I).

The assistance of a grant from the National Science Foundation is gratefully acknowledged.

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[6] F. R. Mayo, W. B. Hardy and C. G. Schultz, THIS JOURNAL, **63**, 433 (1941).

[7] (a) It should be noted that the slower rate of oxime formation of II as compared to 2-methoxy-5-methylacetophenone is ascribed to steric interference by the methyl group in II. The rates of hydrolysis of the corresponding benzoates also are cited; J. Jacques and L. C. Binh, *Compt. rend.*, **244**, 211 (1957). (b) Apparently the carbonyl group also contributes to this steric inhibition since it has been found that 5,6,7-trimethoxyindanone is not cleaved by hydrogen bromide at room temperature; W. J. Horton and B. W. Rossiter, *J. Org. Chem.*, **23**, 488 (1958).

[8] This influence of electrophilic groups was reported previously in the cleavage of naphthol ethers[4] and anisoles.[5]

[9] G. K. Hughes, N. K. Matheson, A. T. Norman and E. Ritchie, *Australian J. Sci. Res., Ser. A*, **5**, 207 (1952).

[10] L. A. Wiles and L. C. Thomas, unpublished work cited in L. A. Wiles, *Chem. Revs.*, **56**, 353 (1956).

[11] The $\Delta m\mu = \lambda m\mu$(*o*- or *m*-methylresacetophenone) $-$ $\lambda m\mu$ (resacetophenone); D. J. Cram and F. W. Cranz, THIS JOURNAL, **72**, 595 (1950).

TABLE II

ULTRAVIOLET ABSORPTION DATA

Acetophenone	Primary band, mμ (log ε)		Secondary band, mμ (log ε)		Δmμ, Prim.	Δmμ, Second.
Parent	244 (4.08)		278 (3.06)		..	..
o-CH_3O[a]	246 (4.06)		305 (3.58)		2	27
o-HO[a]	251 (3.97)		327 (3.50)		7	49
m-CH_3O[b,c]	249 (3.90)		307 (3.38)		5	29
m-CH_3[d]	249 (4.00)		289 (3.10)		5	11
	Found	Calcd.	Found	Calcd.		
2,5-$(CH_3O)_2$	250 (3.80)	251	336 (3.59)	334		
2,3-$(CH_3O)_2$	249 (3.77)	251	305 (3.29)	334		
2-HO-5-CH_3O[e]	256 (3.87)	256	355 (3.58)	356		
2-HO-3-CH_3O	262 (3.99)	256	341 (3.45)	356		
2-CH_3O-5-CH_3	251 (3.89)	251	318 (3.55)	316		
2-CH_3O-3-CH_3[f]	247 (3.89)	254	293 (3.20)	316		
2-HO-5-CH_3	255 (4.03)	256	338 (3.55)	338		
2-HO-3-CH_3[g]	258 (4.05)	256	333 (3.53)	338		

[a] Absorption data taken from R. A. Morton and A. L. Stubbs, *J. Chem. Soc.*, 1347 (1940). The solvent was ethanol. [b] This and the remaining values as well as acetophenone were measured in 1:1 (vol.) ethanol–water. [c] Reported λ_{max}^{alc} 2185, 2490 and 3085 Å. (ε 16600, 7000 and 3500); N. A. Valyashko and A. E. Lutsky, *J. Gen. Chem. U.S.S.R.*, **21**, 1029 (1951); λ_{max}^{ether} 246 and 304 mμ (ε 8500 and 2800); H. Dannenberg, *Z. Naturforsch.*, **4b**, 327 (1949). [d] Prepared by E. J. Fuller; b.p. 100–102° (15 mm.); reported b.p. 101–104° (20 mm.); G. Baddeley, *J. Chem. Soc.*, S229 (1949). [e] M.p. 48–49°; reported m.p. 51–52°; S. v. Kostanecki and V. Lampe, *Ber.*, **37**, 773 (1904). [f] B.p. 116–117° (14 mm.); reported b.p. 115–116° (12 mm.); K. v. Auwers, M. Lechner and H. Bundesmann, *ibid.*, **58B**, 42 (1925). [g] B.p. 111–112° (15 mm.); reported b.p. 106–107° (10.5 mm.); R. Anschutz and M. E. Scholl, *Ann.*, **379**, 333 (1911).

Experimental[12]

Cleavage of 2,3-Dimethoxyacetophenone.—Glacial acetic acid which had been refluxed for 10 hr. with 1% of its weight of chromium oxide and distilled was refluxed with tetraacetyl diborate[13] as reported[14] and distilled using a 40-cm. Vigreux column. The center half of the distillate was collected. Hydrogen bromide, produced by warming a commercial 30% acetic acid solution, was passed over copper turnings to remove free bromine and thence into anhydrous acetic acid protected from moisture. A second method utilized pure hydrogen bromide from a tank. The gas was passed over anhydrous calcium sulfate and thence into acetic acid. This stock solution of hydrogen bromide–acetic acid (10%) acquired a pale yellow color on standing due to the liberation of bromine. The amount of bromine present was too small for iodometric determination and such solutions gave rate constants identical to those found with colorless hydrogen bromide–acetic acid.

The hydrogen bromide–acetic acid was standardized by titration of 1 ml. in 200 ml. of 0.05 *N* nitric acid with 0.1 *N* silver nitrate using a silver electrode–glass electrode system and a Beckman model G *p*H meter. The end-point (120 mv.) was determined by titration of known samples of sodium bromide in 0.05 *N* nitric acid containing 1 ml. of acetic acid. The point of maximum deflection (120 mv.) checked the stoichiometric end-point in the titration of the known samples.

Individual kinetic determinations were made by combining a known weight of I in a volumetric flask at thermal equilibrium with equilibrated hydrogen bromide–acetic acid solution from a pipet and diluting with equilibrated anhydrous acetic acid. The time, t_0, was taken at the point of addition of the hydrogen bromide–acetic acid. The samples were mixed and held at 25.15 ± 0.05° throughout the run. Samples for analysis (1 ml.) were pipetted at intervals into 1:1 (vol.) ethanol–water in 100-ml. volumetric flasks and again diluted 100-fold with the same solvent for spectrophotometric analysis. Absorbances of the diluted samples were determined at 341 and 305 mμ. The solution of two simultaneous equations gave the concentration of each component. The sum of the concentrations was in good agreement with the amount of material known to be present at zero time thus indicating the absence of side reactions.

Compound I prepared as reported[2a] boiled at 146–147° (14 mm.). The absorbances were linear between 0.237 and 0.032 mmole. 2-Hydroxy-3-methoxyacetophenone[2a] after five crystallizations from methanol followed by sublimation melted at 52–53° (cor.), reported[15] m.p. 53–54°. The absorbance of either band was linear between 0.237 and 0.032 mmole.

In a similar manner II, 2,3-dimethoxy-5-bromo- and 2,3-dimethoxy-5-nitroacetophenone cleavages were studied at 25.15°. The rate constants are given in Table I. In compounds lacking a 3-substituent, *o*-methoxy-, 2,5-dimethoxy- and 2-methoxy-5-methylacetophenone, spectrophotometric analysis was not satisfactory due to absorption by unknown side products.

In qualitative experiments similar to those reported,[2a] Compound I was allowed to stand for 4.5 hr. in *ca.* 5% hydrogen chloride–acetic acid. No base-soluble material was obtained. A solution of 0.9 g. of I in 20 ml. of acetic acid was added to 1.8 ml. of 70% perchloric acid and 5 ml. of acetic anhydride. After standing at room temperature for 4.5 hr., 82% of I was recovered as the oxime. No phenolic compound was obtained. Similarly sulfuric acid–acetic anhydride–acetic acid gave only traces of a phenol.

2-Methoxy-5-methylacetophenone.—*p*-Cresyl methyl ether on acylation in polyphosphoric acid gave the acetophenone (74%), b.p. 121–123° (7 mm.), reported[16] b.p. 120.5° (7 mm.).

The oxime, recrystallized from ethanol melted at 89.5–91.0°.

Anal. Calcd. for $C_{10}H_{13}O_2N$: C, 67.02; H, 7.31. Found: C, 67.39; H, 7.48.

2-Hydroxy-5-methylacetophenone.—Hydrogen bromide acetic acid[2a] on the above methyl ether gave phenolic material (6.6%), m.p. 46–47.5° (cor.), reported[17] m.p. 45–46°.

5-Bromo-2-hydroxy-3-methoxyacetophenone.—A solution of 14 g. of 2-hydroxy-3-methoxyacetophenone in 250 ml. of 1:1 aqueous ethanol containing 20 g. of sodium bromide was treated with stirring at 25° with 5 ml. of bromine. The solution was diluted with 25 ml. of water and the precipitate was filtered and washed with aqueous sodium bisulfite. After crystallization from ethanol 10 g. of pale yellow crystals, m.p. 108–109°, was obtained. The ultraviolet spectra gave $\lambda_{max}^{alc-water}$ 264 mμ (log ε 3.84), 347 mμ (log ε 3.47).

Anal. Calcd. for $C_9H_9O_3Br$: C, 44.10; H, 3.70; Br, 32.61. Found: C, 44.17; H, 3.82; Br, 33.1.

5-Bromo-2,3-dimethoxyacetophenone.—5-Bromo-2,3-dimethoxybenzoic acid,[18] m.p. 121–124°, was converted to the acid chloride and thence to the acetophenone using sodiomalonic ester.[19] The fraction boiling at 139° (0.48 mm.) −149.5° (0.65 mm.) (19.5 g., 49.5%) crystallized at once to a nearly colorless solid, m.p. 52.5–64°. After crystallization four times from cyclohexane-benzene the long thin colorless needles melted at 63.7–64.9°. The ultraviolet spectrum gave $\lambda_{max}^{1:1\ alc-water}$ 311 mμ (log ε 3.36) with an inflection at 256 mμ (log ε 3.64).

Anal. Calcd. for $C_{10}H_{11}O_3Br$: C, 46.35; H, 4.28; Br, 30.84. Found: C, 46.33; H, 4.35; Br, 31.0.

The oxime formed tiny long thin rods from cyclohexane–benzene, m.p. 130.4–132.2°.

Anal. Calcd. for $C_{10}H_{12}O_3NBr$: C, 43.81; H, 4.41; Br, 29.15. Found: C, 43.82; H, 4.46; Br, 29.3.

When 2.59 g. of 5-bromo-2,3-dimethoxyacetophenone was allowed to stand in hydrogen bromide–acetic acid for 4.5 hr.[2a] the alkali-soluble material weighed 0.8 g. (36.2%) m.p. 105–106°, crystallized from cyclohexane (carbon).

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(12) Ultraviolet spectra are given in Table II. The solvent was 1:1 (vol.) ethanol–water. Melting points of analytically pure compounds are corrected.

(13) A. Pictet and A. Geleznoff, *Ber.*, **36**, 2219 (1903).

(14) W. C. Eichelberger and V. K. La Mer, THIS JOURNAL, **55**, 3633 (1933). It has been shown that triacetyl borate of refs. 13 and 14 is $(CH_3CO)_2BOB(OCCH_3)_2$; R. G. Hayter, A. W. Laubengayer and P. G. Thompson, *ibid.*, **79**, 4243 (1957).

(15) T. Reichstein, *Helv. Chim. Acta*, **10**, 397 (1927).

(16) C. R. Noller and R. Adams, THIS JOURNAL, **46**, 1889 (1924).

(17) G. Wittig, *Ber.*, **57**, 88 (1924).

(18) W. Davies, *J. Chem. Soc.*, **123**, 1587 (1923).

(19) A. L. Wilds and L. W. Beck, THIS JOURNAL, **66**, 1692 (1944).

The product did not depress the melting point of 5-bromo-2-hydroxy-3-methoxyacetophenone obtained above.

2-Hydroxy-3-methoxy-5-nitroacetophenone.—At 10–20° a solution of 15 g. of 2-hydroxy-3-methoxyacetophenone in 25 ml. of acetic acid was treated with 6.25 ml. of 70% nitric acid and 5 ml. of acetic acid. Stirring was continued while the temperature rose to 25°. The slurry was poured into 300 ml. of cold water and the solid filtered and washed. The dried yellow crystals weighed 18 g. (95%) and melted at 142–145°. Recrystallization from ethanol–ethyl acetate and from ethyl acetate gave pale yellow rods, m.p. 148.1–149.5°. The ultraviolet spectra gave $\lambda_{\max}^{1:1 \text{ alc-water}}$ 250 mμ (log ϵ 4.18), 338 mμ (log ϵ 3.88).

Anal. Calcd. for $C_9H_9O_5N$: C, 51.19; H, 4.30. Found: C, 51.30; H, 4.29.

The acetate, crystallized from ethanol and finally from benzene–petroleum ether (60–72°), formed long rod-like prisms, m.p. 125.2–126.8°.

Anal. Calcd. for $C_{11}H_{11}O_6N$: C, 52.18; H, 4.38. Found: C, 52.39; H, 4.35.

2,3-Dimethoxy-5-nitroacetophenone.—Methylation of the above acetophenone (8.2 g.) in 65 ml. of anhydrous acetone with 4.5 g. of ignited potassium carbonate and 6 ml. of dimethyl sulfate, refluxed for 4 hr., gave 4.5 g. (53%) of dark brownish-yellow crystals, m.p. 70–80°. Crystallized from methanol, the material melted at 81.2–83.2°. The ultraviolet spectra gave $\lambda_{\max}^{1:1 \text{ alc-water}}$ 295 mμ (log ϵ 3.66), 333 mμ (log ϵ 3.70).

Anal. Calcd. for $C_{10}H_{11}O_5N$: C, 53.33; H, 4.92. Found: C, 53.61; H, 5.19.

Permanganate oxidation gave 2,3-dimethoxy-5-nitrobenzoic acid m.p. 176–178° (cor.), reported[20] m.p. 174–175°.

The oxime, crystallized from dilute ethanol and sublimed at 160–180° (0.15 mm.), was obtained as microscopic long thin pointed prisms, m.p. 165.6–167.9°.

Anal. Calcd. for $C_{10}H_{12}O_5N_2$: C, 50.00; H, 5.04. Found: C, 50.15; H, 5.02.

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(20) C. S. Gibson, J. L. Simonsen and M. G. Rau, *J. Chem. Soc.*, **111**, 68 (1917).

SALT LAKE CITY 12, UTAH

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Ionic Polymerization. IX. The Effect of Water in the Cationic Polymerization of Styrene Catalyzed by Stannic Chloride[1]

BY C. G. OVERBERGER, R. J. EHRIG[2] AND R. A. MARCUS

RECEIVED JUNE 10, 1957

This work was undertaken in order to obtain information on the mechanistic role of water on the polymerization of styrene catalyzed by stannic chloride. The polymerization and molecular weight were studied as a function of the concentration of water and of the other reagents in a nitrobenzene–carbon tetrachloride solvent medium at 25°. Unusually stringent drying conditions and a quantitative measure of water permitted the water content in these experiments to be known with high accuracy and allowed data to be obtained not available from previous work. A high vacuum technique was employed for introduction of all reagents, and the polymerization rate was following dilatometrically The initial rate of the reaction was observed to increase to a maximum and then decrease as the initial concentration of water was increased. The decrease in rate has been attributed partly to heterogeneity. At a constant initial water concentration, the reaction was found to be first order with respect to the stannic chloride concentration between 0.005 and 0.02 *M*, and approximately second order with respect to the monomer concentration between 1 and 3 *M*. The degree of polymerization of the resulting polymer increases with the initial monomer concentration, decreases with the water concentration, and is essentially independent of the catalyst concentration. A reaction mechanism has been proposed to account for these results, in which a monohydrate catalyst–cocatalyst complex is assumed. Termination is postulated to occur by a spontaneous unimolecular process and a bimolecular process involving water. A monomer transfer step is also indicated.

Although it is now generally believed that a cocatalyst is essential in the polymerization of olefins catalyzed by metal halides, very little information is available on the quantitative effects of cocatalysts in cationic polymerization.[3]

A qualitative investigation of the effect of trichloroacetic acid as a cocatalyst on the reaction rate of styrene catalyzed by titanium tetrachloride in hexane and toluene solvents was made by Plesch.[4] The effect of water on the reaction rate for the same monomer and catalyst system in ethylene dichloride solvent also was studied. No molecular weight data were presented in these studies. In particular in only two previous cases has the quantitative effect of water on the rate and molecular weight in cationic polymerization been reported.[5,6] The former work was concerned with the polymerization of isobutene at −78.5° catalyzed by stannic chloride in the presence of ethyl chloride as solvent. Only semi-quantitative molecular weight data were reported. In the latter case,[6] α-methylstyrene was polymerized to low molecular weight polymers (dimers, trimers, etc.) by stannic chloride catalyst in ethyl chloride solvent. Polymerization to obtain high molecular weight material was not studied. The reaction was conducted primarily at 55° at a catalyst–cocatalyst ratio of 1 to 3. Thus, this present work was undertaken in order to obtain knowledge of the polymerization reaction with respect to water as the cocatalyst in the polymerization of styrene to high polymer and to ascertain the mechanistic role of water in the polymerization.

The system chosen for study was the polymerization of styrene catalyzed by stannic chloride in a mixed solvent medium of nitrobenzene–carbon tetrachloride at 25°, since previous work in this Laboratory had provided considerable knowledge about the system. The rate of polymerization was followed dilatometrically, and a high vacuum technique was employed for introduction of the reagents into the dilatometer. Stringent drying of the reagents was employed. In a 30/70% mixture of nitrobenzene–carbon tetrachloride, the dependence

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(1) This is the ninth in a series of papers concerned with ionic polymerization. For the eighth paper, see C. G. Overberger, E. M. Pearce and D. Tanner, THIS JOURNAL, **80**, 1761 (1958).

(2) From the dissertation submitted by R. J. Ehrig to the Graduate School of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(3) For the most recent review of cationic polymerization see D. C. Pepper, *Quart. Revs.*, **8**, 88 (1954).

(4) P. H. Plesch, *J. Chem. Soc.*, 1653, 1659, 1662 (1953).

(5) R. G. W. Norrish and K. E. Russell, *Trans. Faraday Soc.*, **48**, 91 (1952).

(6) F. S. Dainton and R. H. Tomlinson, *J. Chem. Soc.*, 151 (1953).