

[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA, CHARLOTTESVILLE, VA.]

The Base-catalyzed Addition of Methanol to Dibenzoylthylenes¹BY THOMAS I. CROWELL, GROVER C. HELSLEY,² ROBERT E. LUTZ AND WILLIAM L. SCOTT³

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The kinetics of the addition of methanol to the double bond of dibenzoylthylenes, measured in triethylamine buffers, acetate buffers and sodium methoxide solutions over the pH range 6 to 14, showed specific methoxide-ion catalysis and also slow uncatalyzed addition. Nine *p*-substituted dibenzoylthylenes yielded a Hammett plot approximately linear in $\sigma_1 + \sigma_2$. This result is discussed in terms of the expected effect of two substituents, each acting on two reaction sites.

Nucleophilic additions to carbon-carbon double bonds are not nearly as well documented as additions in which protonation or other electrophilic attack is the first step. Detailed kinetic studies in buffer solutions include the addition of trinitromethane to β -nitrostyrene⁴; the addition of aniline to 2,4-dinitrofluorobenzene as a step in aromatic substitution⁵; the hydration of a β -nitrostyrene, prior to alkaline cleavage⁶; and the addition of water to the monofumarate ion.⁷ The last two reactions share a novel addition of water to a double bond in nearly neutral solution, in one case due to electron withdrawal by the nitro group and in the other to intramolecular catalysis.

methoxide, to form methoxydibenzoylthane (IV).⁹ This paper describes a more thorough investigation of the kinetics of the addition, including the effect of substituents in either or both of the benzene rings upon the rate.

Kinetics and Mechanism

It was necessary to measure the rate as a function of both the methoxide-ion concentration and the total base concentration, because a slow reaction in pure methanol suggested the possibility of general base catalysis. The conditions used to achieve the various pH values are shown in Table I.

The reactions, which were carried out with very low concentrations of dibenzoylthylenes (I) and analyzed spectrophotometrically at 269 m μ , followed a first-order course at high pH. Equilibrium was established at 92% reaction,⁹ a fact substantiated by running the reverse reaction starting with the methanol adduct IV in sodium methoxide solution. The equilibrium position did not depend upon the sodium methoxide concentration nor was the spectrum of the reaction mixture changed by acidification.

TABLE I
RATE AS A FUNCTION OF pH

Reagent	pH	<i>k</i> , min. ⁻¹
HCl, 4×10^{-5} M	4.4	2.1×10^{-5}
HAc, 0.02 M	6	5×10^{-5}
Pure CH ₃ OH	8	1.8×10^{-5}
HAc, 0.0020 M; NaAc, 0.00021 M	8.5 ^a	3×10^{-5}
HAc, 0.12 M; NaAc, 0.12 M	8.6 ^b	2×10^{-4}
HAc, 0.024 M; NaAc, 0.024 M	8.9 ^b	2×10^{-4}
HAc, 0.0024 M; NaAc, 0.0024 M	9.5 ^b	2×10^{-4}
Et ₃ N, 0.0318 M; Et ₃ NH ⁺ , 0.0318 M	10.0 ^c	10^{-3}
NaOCH ₃ , 1.34×10^{-4} M	12.12	0.0219
Et ₃ N, 0.0229 M	12.18	.0293
NaOCH ₃ , 1.58×10^{-4} M	12.20	.0299
NaOCH ₃ , 1.91×10^{-4} M	12.28	.0389
Et ₃ N, 0.0635 M	12.40	.0510
Et ₃ N, 0.0716 M	12.43	.0507
NaOCH ₃ , 2.68×10^{-4} M	12.43	.0520
Et ₃ N, 0.143 M	12.58	.0682
Et ₃ N, 0.160 M	12.60	.085
NaOCH ₃ , 7.7×10^{-4} M	12.88	.17
NaOCH ₃ , 7.7×10^{-3} M	13.88	2.56
NaOCH ₃ , 7.7×10^{-2} M	14.88	Fast

^a M. Kilpatrick, and R. D. Eanes, *J. Am. Chem. Soc.*, **75**, 586 (1953). ^b If ionic strength affects the ion product of methanol to the same degree as the dissociation constant of acetic acid, the methoxide ion concentration is the same for these three runs. ^c J. R. Schaefgen, M. S. Newman and F. H. Verhoek, *J. Am. Chem. Soc.*, **66**, 1847 (1944). The value 1.0×10^{-16} was used for the ion product of methanol.

Carbonyl groups conjugated with a double bond will render it quite susceptible to nucleophilic attack, as in the dibenzoylacetylenes. A kinetic study of the addition of HSCN, HBr and HI to diacetylacetylene showed the rate to be proportional to the anion concentration.⁸ *trans*-Dibenzoylthylenes (I) has been found to react with methanol, in the presence of sodium

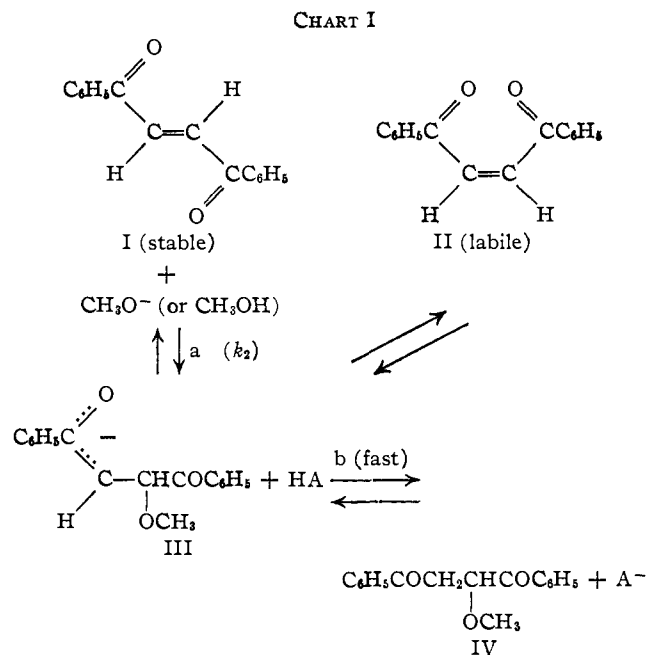


Figure 1 is a plot of log *k* vs. pH for I \rightarrow IV. Acid and base catalysis are apparent, with an uncatalyzed solvolysis showing up near neutrality. The reaction in acid solution, however, is not well enough understood to permit the calculation of rate constants; for example, the spectrum of IV does not immediately appear, though the peak of I at 269 m μ decreases rapidly. The curve in Fig. 1 follows the equation k (min.⁻¹) = $1.8 \times 10^{-5} + 182[\text{OCH}_3^-]$. The second-order constant 182 l. mole⁻¹ min.⁻¹ was obtained as the slope

(1) This work received some of its support from the Office of Ordnance Research, U. S. Army.

(2) Philip Francis du Pont Fellow, 1956-1957. M. S. Thesis University of Virginia, 1957.

(3) National Science Foundation Research Participant, 1961.

(4) J. Hine and L. A. Kaplan, *J. Am. Chem. Soc.*, **82**, 2915 (1960).

(5) J. F. Bunnett and J. J. Randall, *ibid.*, **80**, 6020 (1958).

(6) T. I. Crowell and A. W. Francis, Jr., *ibid.*, **83**, 591 (1961).

(7) M. L. Bender and K. A. Connors, *ibid.*, **84**, 1980 (1962).

(8) V. G. Ostroverkhov, *Ukr. Khim. Zh.*, **23**, 474 (1957); *Chem. Abstr.*, **52**, 6196a (1958).

(9) R. E. Lutz and C.-K. Dien, *J. Org. Chem.*, **21**, 551 (1956).

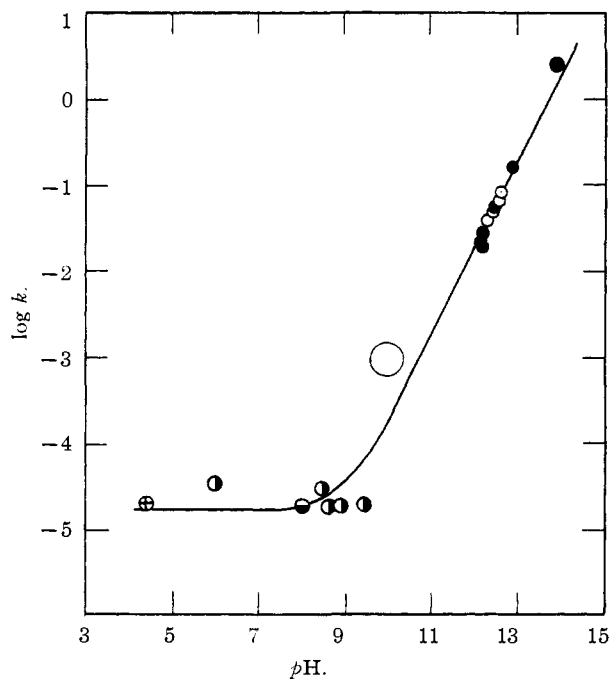


Fig. 1.—pH-rate profile: ●, solvent (methanol) only; ○, acetate buffers; ○, triethylamine buffers; ●, sodium methoxide; ⊕, hydrochloric acid.

of a plot of k vs. $[\text{OCH}_3^-]$ from pH 12.12 to 12.60, the region of the most accurate runs. The satisfactory fit where acid catalysis is negligible indicates strong specific methoxide-ion catalysis superimposed on the uncatalyzed reaction. General base catalysis was not detected. A satisfactory mechanism is rate-controlling attack (a, Chart I) of methoxide ion competing with an analogous but much slower concurrent attack by methanol. The subsequent protonation b must be fast, since there is no general acid catalysis.

One irregularity in the kinetics should be mentioned: in the acetate buffers and in methanol, there was a short period of more rapid reaction which then tapered off to the long, strictly first-order part. Neither increases in the water content of the methanol nor repeated recrystallization of I changed the course of the reaction. The phenomenon was especially puzzling because almost any mechanistic explanation would require general catalysis or an accentuation of the effect at high pH , neither of which was observed. It was found, however, that when the reaction was carried out with more concentrated dibenzoyl ethylene ($5 \times 10^{-3} M$) and diluted for spectral analysis, this initial deviation from first-order kinetics entirely disappeared. We therefore attribute it to catalysis by the alkali in the glass walls of the flask.

Effect of Substituents

Nine dibenzoyl ethylenes V were prepared with different pairs of substituents, X and Y, in the two p -positions. The rates of methanol addition in triethylamine solutions are given in Table II. A linear Hammett plot, Fig. 2, is obtained when $\sigma_X + \sigma_Y$ is the abscissa: the slope, ρ , is 1.00. (The set of six symmetrically substituted compounds, including di-(4-chloro-3-methylbenzoyl)-ethylene, where all σ -constants were added,¹⁰ must then give a normal Hammett plot, linear in σ , with $\rho = 2.00$).

The sum of two σ -constants has been used before to correlate reaction rates at a center affected by two symmetrically located substituents.¹¹ It was by no

(10) See R. M. Stone and D. E. Pearson, *J. Org. Chem.*, **26**, 257 (1961).

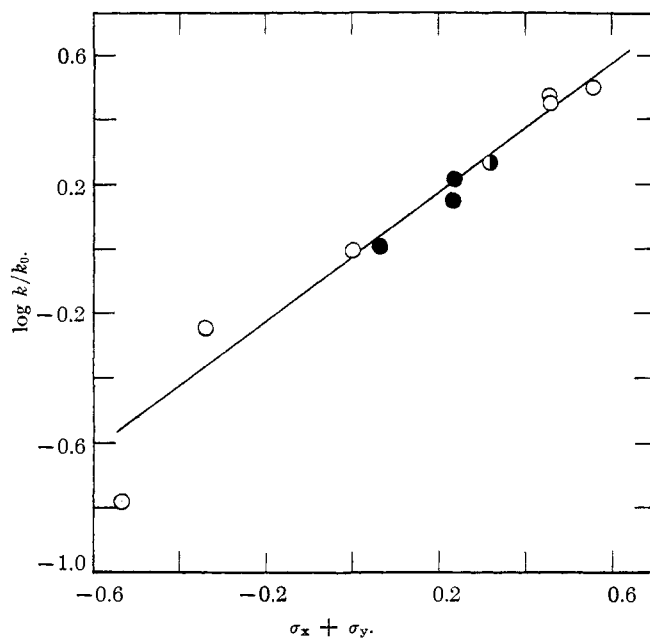
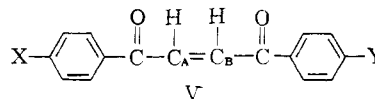


Fig. 2.— $\log k/k_0$ vs. $\sigma_X + \sigma_Y$: ○, X = Y; ○, X = Y = R; ●, X \neq Y.

means a foregone conclusion, however, that this simple correlation would serve for dibenzoyl ethylene, as the following analysis will show.

Two carbon atoms, C_A and C_B , are available as reaction sites. Alternatively, reaction could occur at a carbonyl group with rapid rearrangement. Each is influenced by both substituents, X and Y. Let the rate



constant for reaction at C_A be k_A in general and k_A^0 in the parent compound, where X = Y = H; similarly for C_B . Furthermore, suppose the effect of X on k_A follows a Hammett plot of slope ρ_A and the effect of X on k_B is additive but decreased by a falloff factor α .¹² Then the rate of attack at C_A will be given by

$$\log(k_A/k_A^0) = \rho_A(\sigma_X + \alpha\sigma_Y)$$

and the rate at C_B by

$$\log(k_B/k_B^0) = \rho_A(\sigma_Y + \alpha\sigma_X)$$

The observed rate constant k for reaction at both sites will be $k_A + k_B$, and using the exponential forms together with the fact that $k^0 = k_A^0 + k_B^0 = 2k_A^0$

$$k/k^0 = 1/2 [10^{\rho_A(\sigma_X + \alpha\sigma_Y)} + 10^{\rho_A(\sigma_Y + \alpha\sigma_X)}] \quad (2)$$

If X = Y, eq. 2 reduces to $k/k^0 = 10^{\rho_A\sigma(1 + \alpha)}$, a linear Hammett plot. Even if X \neq Y, linearity will still be observed if $\alpha = 1$, that is if C_A and C_B are equally affected by a substituent on one of the rings, and eq. 2 becomes $k/k^0 = 10^{\rho_A(\sigma_X + \sigma_Y)}$. However, for any other value of α , dibenzoyl ethylenes with two different substituents will not fall on a linear plot of $\log k$ vs. $\sigma_X + \sigma_Y$. This is easily seen for the case $\alpha = 0$, where X has no effect on C_B and Y none on C_A . Here the two halves of the molecule act independently and an average value, $k/k^0 = [10^{\rho_A\sigma_X} + 10^{\rho_A\sigma_Y}]$ is obtained.

The predicted variation in reaction rate with α for the present study is given in Table III for the unsym-

(11) C. G. Swain, W. H. Stockmayer and J. T. Clarke, *J. Am. Chem. Soc.*, **72**, 5426 (1950); J. D. McCullough and M. K. Barsh, *ibid.*, **71**, 3029 (1949); S. J. Cristol, *ibid.*, **67**, 1494 (1945).

(12) This factor for interposition of $-\text{COCH}=\text{C}$ might be the same for all reactions at C_B ; H. H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953); *J. Am. Chem. Soc.*, **81**, 3288 (1959).

TABLE II
RATE AND ABSORPTION DATA FOR *p*-SUBSTITUTED DIBENZOYLETHYLENES

X	Y	λ_{\max} , $\mu\mu^a$	ϵ_{\max}^b	λ_{\max} , $\mu\mu$ in NaOCH ₃	ϵ_{\max}^b	λ_{\max} , $\mu\mu$ methoxyethane	ϵ_{\max}^b	k_2 , $\text{mole}^{-1} \text{min.}^{-1}$
OCH ₃	OCH ₃	322	2.12	282	2.72	282	3.40	299
CH ₃	CH ₃	295	2.03	257	3.02	104
H	H	269	1.96	246 ^c	2.38	246 ^c	2.48 ^c	181
Br	Br	288	2.24	259	3.51	259	3.82	519
Cl	Cl	282	2.11	258	3.19	258	3.38	544
I	I	305	2.44	272	3.24	571
R ^d	R	290	1.96	259	3.02	339
CH ₃	Br	293	2.02	259	3.19	187
H	Cl	275	2.02	253	2.74	258
H	Br	278	2.06	255	2.69	307

^a For the long wave length peak. ^b $\times 10^{-4}$. ^c Ref. 9. ^d R = 4-chloro-3-methyl.

metrically substituted compounds. We know from Fig. 2 that $\rho_A(1 + \alpha) = 2.00$, so for any assumed α , ρ_A may be calculated as in the second column. In the third column is the calculated k/k^0 for mono-*p*-bromodibenzoyl-ethylene and mono-*p*-chlorodibenzoyl-ethylene in both of which $\sigma_X = 0$ and $\sigma_Y = 0.23$. The last column gives the calculated k/k^0 for *p*'-bromo-*p*-methyl-dibenzoyl-ethylene, $\sigma_X = -0.17$, $\sigma_Y = 0.23$.

TABLE III
CALCULATED k/k_H FOR MONO-*p*-CHLORODIBENZOYLETHYLENE, MONO-*p*-BROMODIBENZOYLETHYLENE AND *p*-BROMO-*p*'-METHYLDIBENZOYLETHYLENE^a

α	ρ_A	k/k_H (<i>p</i> -Cl) ^b	k/k_H (<i>p</i> -Br- <i>p</i> '-CH ₃)
0	2.00	1.94	1.67
0.1	1.82	1.85	1.48
.2	1.66	1.80	1.37
.3	1.54	1.77	1.29
.4	1.44	1.74	1.24
.5	1.33	1.72	1.20
.6	1.26	1.71	1.18
.7	1.18	1.71	1.16
.8	1.12	1.70	1.15
.9	1.06	1.70	1.15
1.0	1.00	1.70	1.15
2.0	0.67	1.73	1.20
3.0	0.50	1.75	1.27
∞	0	1.94	1.67

^a From eq. 2, assuming $\rho_A(1 + \alpha) = 2.00$. ^b This column also represents *p*-Br since $\sigma_X = 0$ and $\sigma_Y = 0.23$ for both.

The observed values of k/k^0 for the above three unsymmetrically substituted compounds are, respectively, 1.69, 1.42 and 1.03. Although more data would be desirable, the reaction seems to be more nearly characterized by $\alpha = 0.5-1$ than $\alpha = 0$. There seems no reason why α should not be greater than 1 due to specific resonance effects on C_B by X. Our data are insufficient to separate resonance and inductive effects.

The groups X and Y, then, each exert appreciable influence on both reaction sites, or else affect the double bond as a whole, where reaction occurs. Recent calculations,¹⁸ however, suggest that electrophilic attack to form a π -complex is more likely than an analogous free-radical attack; possibly nucleophilic attack is more oriented toward bond formation with one particular carbon atom.

Steric Effects

cis-Dibenzoyl-ethylene reacted more slowly with sodium methoxide: a preliminary value of k_2 is 4 l. mole⁻¹ min.⁻¹. A similar relationship in the reactivities of the *cis*- and *trans*-chalcones toward hydroperoxide

ion was observed by Lutz and Weiss.¹⁴ Their general explanation, in terms of steric interference with the planarity of conjugated systems in the *cis* compound, may also be applicable here. This possibility is strengthened by the fact that *trans*-dimesityl-ethylene also reacts quite slowly.

Isomerization of *cis*-dibenzoyl-ethylene to *trans* prior to addition was not detected; the ratio of addition rates, 4/180, would preclude accumulation of an appreciable quantity of *trans* initially in any case. Moreover, the plausible isomerization II \rightarrow III \rightarrow I could not be a significant path to addition within the mechanistic scheme shown, since we have concluded that the protonation b is fast. Later, as equilibrium is approached, *trans*-dibenzoyl-ethylene will of course be formed in the same proportion as though it had been the starting material.

Although substituted *cis*-dibenzoyl-ethylenes were not studied, they would be of considerable interest because the complexity of steric interactions might lead to substituent effects quite different from those described in this paper for the simpler *trans* isomers.

Experimental¹⁵

cis- and *trans*-Dibenzoyl-ethylene,¹⁶ mono-*p*-bromodibenzoyl-ethylene,¹⁷ di-(4-chloro-3-methylbenzoyl)-ethylene,¹⁸ di-(*p*-chlorobenzoyl)-ethylene,¹⁶ dimesityl-ethylene,¹⁶ di-(*p*-methylbenzoyl)-ethylene,¹⁶ di-(*p*-bromobenzoyl)-methoxyethane¹⁹ and 1,2-dibenzoylmethoxyethane¹⁹ were prepared as in the references given. New compounds and those prepared by new methods are given below.

trans-2-Methoxy-1,4-di-(4-methoxyphenyl)-butane-1,4-dione.—Following the method of Lutz and Dien,⁹ a solution of 3 g. of di-(4-methoxybenzoyl)-ethylene and 0.1 g. of sodium hydroxide in 800 ml. of methanol was allowed to stand for 1 hour and was poured into 400 ml. of ice-water. Extraction with ether gave an oil which crystallized from methanol; 0.5 g. (15%), m.p. 80–81°.

Anal. Calcd. for C₁₈H₂₀O₆: C, 69.49; H, 6.18. Found: C, 69.69; H, 6.54.

The preparation of *trans*-2-methoxy-1,4-di-(4-chlorophenyl)-butane-1,4-dione¹⁹ was direct as follows: a solution of 0.5 g. of di-(*p*-chlorobenzoyl)-ethylene¹⁶ in 450 ml. of methanol was treated with 20 ml. of 0.2% methanolic sodium hydroxide at room temperature. After standing for 10 minutes it was neutralized with glacial acetic acid (3 drops), evaporated to 20 ml. and filtered to remove unchanged starting material which had crystallized. Further evaporation and addition of 1 ml. of methanol gave a small yield of the methoxy compound, m.p. 61.5–62° (identified¹⁹).

trans-Di-(4-iodophenyl)-2-butene-1,4-dione.—Preparation was by a modification²⁰ of the standard procedure.¹⁶ A mixture of 18 g. of fumaryl chloride and 31 g. of aluminum chloride in 150 ml. of ethylene dichloride was stirred for 30 minutes at room temperature and the solution of the soluble complex decanted. To this complex under stirring at 100° was added dropwise 48 g. of iodobenzene. Hydrolysis and working up gave light yellow crystals from ethanol-benzene; 17.3 g. (30%), m.p. 234–234.5°.

Anal. Calcd. for C₁₆H₁₀I₂O₂: C, 39.37; H, 2.07. Found: C, 39.39; H, 1.99.

The *p*-iodo structure was proved by alkaline permanganate oxidation to *p*-iodobenzoic acid (identified by mixture m.p. with an authentic sample).

trans-1-(4-Bromophenyl)-4-(4-tolyl)-2-butene-1,4-dione was prepared by the earlier procedures^{17, 21} from *trans*-*p*-bromobenzoyl-acrylyl chloride, as: a mixture of the crude acid chloride and phosphorus oxychloride from 32 g. of the *trans*-acid and 20.5 g. of phosphorus pentachloride, 300 ml. of toluene and 20 g. of aluminum chloride was heated for 1 hour at 55–60°. After hydrolysis and work-up, the product crystallized upon addition of petroleum ether-pentane to the toluene solution; 6 g. (14%), m.p. 157–158° (yellow).

Anal. Calcd. for C₁₇H₁₄BrO₂: C, 62.02; H, 3.99. Found: C, 62.11; H, 3.85.

(14) R. E. Lutz and J. O. Weiss, *ibid.*, **77**, 1814 (1955).

(15) All melting points are corrected.

(16) J. B. Conant and R. E. Lutz, *J. Am. Chem. Soc.*, **45**, 1303 (1923).

(17) E. P. Kohler and D. W. Woodward, *ibid.*, **58**, 1933 (1936).

(18) J. B. Conant and R. E. Lutz, *ibid.*, **47**, 881 (1925).

(19) R. E. Lutz, *ibid.*, **51**, 3019 (1929).

(20) G. Baddeley, G. Holt and S. M. Makar, *J. Chem. Soc.*, 3289 (1952).

(21) D. Papa, *et al.*, *J. Am. Chem. Soc.*, **70**, 3358 (1948).

(13) S. Sato and R. J. Cvetanovic, *J. Am. Chem. Soc.*, **81**, 3223 (1959).

trans-1-(4-Chlorophenyl)-4-phenyl-2-butene-1,4-dione.—A mixture of 14.4 g. of phenylglyoxal, 15.4 g. of *p*-chloroacetophenone and 250 g. of acetic anhydride was refluxed for 2 hours and hydrolyzed with ice-water. The precipitated oil was crystallized from ethanol; 4 g. (15%), m.p. 120.5–121.5° (yellow).

An improved preparation²² of di-(*p*-methoxybenzoyl)-ethylene is: To a stirred mixture of 114 g. of anhydrous aluminum chloride in 550 ml. of benzene at 70° was added 68 g. (0.63 mole) of anisole, and this was followed by dropwise addition over 4–5 min. of a mixture of 60 g. (0.39 mole) of fumaryl chloride and 40 g. (0.37 mole) of additional anisole. Refluxing occurred and was continued for an additional 10 min. The mixture was then cooled and poured into ice containing 30 ml. of concd. hydrochloric acid. The resulting suspension of the bulk of the product (an orange solid) was filtered, and a small additional crop was obtained from the benzene solution; yield, nearly pure, 44 g. (41%). Recrystallization was from butanone–ethanol mixture; m.p. 168–168.5° (lit.¹⁶ 165.5°).

Di-(*m*-nitrobenzoyl)-ethylene. (1,4-Di-3-nitrophenyl-2-butene-1,4-dione).—The method for nitrating β -benzoylacrylic acid to its 3-nitro derivative²³ was used. A solution of 11 g. of 1,2-dibenzoyl-ethylene was made in 25 ml. of fuming nitric acid at 0°, and was poured into ice-water. The product was washed and crystallized from ethanol–benzene mixture; yield 6 g. (40%), m.p. 205–205.5° (pale yellow).

Anal. Calcd. for C₁₈H₁₀N₂O₆: C, 58.85; H, 3.09. Found: C, 58.80; H, 2.99.

Aqueous alkaline permanganate oxidation gave a little over one equivalent of *m*-nitrobenzoic acid (identified).

An isomer was obtained by evaporation of the solvent from the above crystallizations; m.p. 129–130°.

Anal. Calcd. for C₁₈H₁₀N₂O₆: C, 58.85; H, 3.09. Found: C, 59.10; H, 2.93.

The nitro compounds were too insoluble in methanol for kinetic study by the procedure used for the rest of the series.

(22) (a) J. D. Hutcheson, (b) N. H. Shearer, Theses, University of Virginia, 1933, 1944, resp.

(23) M. T. Bogert and J. J. Ritter, *J. Am. Chem. Soc.*, **47**, 526 (1925).

Procedure.—A solution about 5×10^{-5} *M* in the dibenzoyl-ethylene, also containing the buffer components, was prepared using reagent grade methanol as solvent. All reactions were run at 25.0°. The optical density at the wave length of maximum absorption of the substrate was determined at intervals.

The spectra of the reaction mixtures from *p*-methoxy-, *p*-bromo- and *p*-chlorodibenzoyl-ethylene, when compared with the spectra of the methoxyethanes, prepared by addition of methanol as described above, showed that equilibrium was reached at about 90% reaction, as in the parent compound.⁹ Any effect of substituents on the equilibrium constant was smaller than the experimental error. The kinetic runs were plotted by calculating the concentration of dibenzoyl-ethylene from the optical density and the known absorptivities of reactant and product, and using this concentration in the simple first-order equation, $\ln A_0/A = kt$, for the first 25% reaction. Values of k_2 were then obtained by dividing k by the methoxide-ion concentration, except in the more detailed study of the parent dibenzoyl-ethylene. For the remaining six compounds of Table II, the products were not prepared but their absorptivities were estimated from values for similar compounds and from the observed equilibrium mixture. It should be noted that the ratio of the two isomeric addition products from each unsymmetrical dibenzoyl-ethylene was not measured.

After standing from 1 to 4 months, *trans*-dibenzoyl-ethylene in methanol or in triethylamine–triethylammonium chloride buffers, and *cis*-dibenzoyl-ethylene in acid solutions show spectral evidence of the cyclic methoxydiphenylfuran, known to be formed under such conditions.²⁴ Our observation that cyclization to this stable product occurs after the faster dibenzoylmethoxyethane formation is in accord with the results of Bailey and Kelley,^{24b} who started with the latter compound and isolated both dibenzoyl-ethylene and methoxydiphenylfuran after refluxing with methanolic triethylamine hydrochloride and hydrogen chloride.

(24) (a) P. S. Bailey and R. E. Lutz, *ibid.*, **69**, 498 (1947); (b) P. S. Bailey and J. T. Kelley, *ibid.*, **70**, 3442 (1948); (c) R. E. Lutz and M. G. Reese, *ibid.*, **81**, 3397 (1959).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN 1, N. Y.]

Solvent Effects in Cationic Polymerization and Copolymerization¹

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The cationic reactivity ratios for the copolymerization of *p*-chlorostyrene and isobutylene and for chloroprene and styrene were determined in various solvents. The results obtained in hydrocarbon solvents strongly indicate that the solvation of the growing ion pair by the more polar monomer was the predominant effect.

Monomer reactivity ratios have been established to be generally independent of the dielectric constant of the solvent or the initiator in free radical copolymerizations. The effect of temperature on the reactivity ratios has also been found to be negligible in radical polymerizations. It was interesting to investigate how far these monomer reactivity ratios are affected by changes in solvent in cationic-initiated copolymerizations where ions or ion pairs are involved. A preliminary communication on our findings has been reported earlier.

Small variations in the values of r_1 and r_2 were reported by Florin⁴ in the cationic copolymerization of styrene and 3,4-dichlorostyrene using different initiators. Changes were also observed when nitrobenzene was used as solvent instead of carbon tetrachloride. No attempt was made to explain these observations and since some of the polymerizations were heterogeneous, interpretation was difficult. Overberger, *et*

al.,⁵ did not observe any major changes in the reactivity ratios of styrene and *p*-chlorostyrene copolymerizations in mixed solvents of nitrobenzene and carbon tetrachloride. Neither was any change observed for the r_1 and r_2 values of these monomers using different initiators such as titanium tetrachloride and stannic chloride.⁶ The cationic copolymerization of α -methylstyrenes with 2-chloroethyl vinyl ether in benzene as well as nitrobenzene solvents has been reported recently by Marvel.⁷ Only in the case of α -methylstyrene itself was some change observed in the maximum reactivity ratios.

Results and Discussion

One of the objections that can be raised to the use of mixed solvents is that the measured dielectric constant of the mixture may not accurately describe the system on a molecular level. To eliminate this possibility it was desirable to measure the reactivity ratios in pure solvents. Isobutylene was copolymerized with *p*-chlorostyrene in different solvents and the results are given in Table I. This particular monomer pair was chosen because of the expected differences in the reactivities of the carbonium ions derived from the

(1) This is the 21st in a series of papers concerned with ionic polymerization; for the previous paper in this series, see G. F. Endres, V. G. Kamath and C. G. Overberger, *J. Am. Chem. Soc.*, **84**, 4813 (1962).

(2) This paper comprises a portion of the Dissertation submitted by V. G. Kamath in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Polytechnic Institute of Brooklyn.

(3) C. G. Overberger and V. G. Kamath, *J. Am. Chem. Soc.*, **81**, 2910 (1959).

(4) R. E. Florin, *ibid.*, **71**, 1867 (1949); **73**, 4468 (1951).

(5) C. G. Overberger, L. H. Arond and J. J. Taylor, *ibid.*, **73**, 5541 (1951).

(6) C. G. Overberger, R. J. Ehrig and D. Tanner, *ibid.*, **76**, 772 (1954).

(7) C. S. Marvel and J. F. Dunphy, *J. Org. Chem.*, **25**, 2209 (1960).