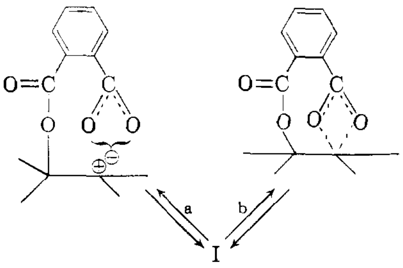
fling in the process by which cyclic phthalate is formed from peroxide and olefin. We see no plausible path for isotopic shuffling in the process of formation of peroxide and exclude the first possibility on this basis. Earlier work[3] has shown that the lactonic *ortho*-ester II and cyclic phthalate I have high thermal stability and are *not* interconverted, excluding the second possibility. The third possibility represents an interconversion that might take place by way of an ion-pair process (a) or a molecular SNi process (b). Although neither of these possibilities is excluded by the evidence at hand, the resistance of simple esters to this type of interconversion[13] and the slowness of isomerization of tosylates under conditions that are far more conducive to ionization[14] do not lend encouragement to the acceptance of alternatives a or b as the mechanism of oxygen transposition.[15] On the other hand, isotopic shuffling in the olefin reaction itself is consistent with kinetic and product evidence.[1] This matter will be discussed in detail in a forthcoming publication in conjunction with additional information bearing on the mechanism of the reaction of phthaloyl peroxide with carbon–carbon unsaturation.



Experimental

Phthaloyl Chloride-O^{18}.—A mixture of 11 g. of phthaloyl chloride (Eastman Kodak Co. white label, redistilled, b.p. 86–88° at 0.1 mm.) and 100 ml. of water containing 1.4 atom % oxygen-18 (Stuart Oxygen Co.) was heated at reflux overnight. From the cooled mixture 9.4 g. of phthalic acid was obtained, dec. p. 207–208°. This material was converted to phthaloyl chloride-O^{18} by means of phosphorus pentachloride.

Phthaloyl peroxide-*carbonyl*-O^{18} was prepared from the above acid chloride by the procedure described previously.[4]

Reaction of Phthaloyl Peroxide-*carbonyl*-O^{18} with *trans*-Stilbene.—This reaction was carried out under two sets of conditions. The oxygen-18 analyses are reported in Table I.

By Direct Reaction.—Peroxide and olefin were heated at reflux in carbon tetrachloride for 16 hr. and worked up as described previously.[3] The cyclic phthalate melted at 206–207° after recrystallization from carbon tetrachloride (reported[3] m.p. 206–207°).

Alkaline hydrolysis of the cyclic phthalate[3] afforded *dl*-1,2-diphenylethanediol of m.p. 119.5–120° after recrystallization from hexane.

After Prior Heating of Phthaloyl Peroxide.—A solution of 1.00 g. of phthaloyl peroxide-*carbonyl*-O^{18} in 100 ml. of carbon tetrachloride was sealed in a flask under nitrogen and heated at 80° for 96 hr. Iodometric analysis of a 5-ml. aliquot indicated only 13% destruction of peroxide in this time period. To the remainder of the phthaloyl peroxide solution was added an equimolar amount of *trans*-stilbene, and the solution was heated at reflux for 18 hr. A 3-ml. portion was evaporated to dryness for spectral analysis. The infrared absorption spectrum of this sample in chloroform was the same as that obtained previously from direct reaction of the peroxide and *trans*-stilbene.[3] The cyclic phthalate was isolated as before, m.p. 206–207°.

Alkaline hydrolysis of the cyclic phthalate afforded *dl*-1,2-diphenylethanediol, m.p. 119.5–120° after recrystallization from hexane.

Acknowledgment.—We are indebted to Professor Myron L. Bender for the oxygen-18 analyses and for his encouragement in this problem.

CAMBRIDGE 39, MASSACHUSETTS

[13] K. B. Wiberg, T. W. Shryne and R. R. Kintner, THIS JOURNAL, **79**, 3160 (1957).

[14] D. B. Denney and B. Goldstein, *ibid.*, **79**, 4948 (1957).

[15] Although processes of the type a and b are considered unlikely under the experimental conditions employed here, these processes may occur under other circumstances.

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

The Thermal Decomposition of Substituted *t*-Butyl N-Phenylperoxycarbamates[1-3]

BY EUGENE L. O'BRIEN, F. MARSHALL BERINGER AND ROBERT B. MESROBIAN[4]

RECEIVED JULY 30, 1958

Addition of *t*-butyl hydroperoxide to substituted phenyl isocyanates gave substituted *t*-butyl N-phenylperoxycarbamates. Their ultraviolet and infrared absorption spectra and their rates of decomposition in toluene over a 30° range of temperatures were measured. First-order rate constants increased with the electron-releasing power of the substituents; a Hammett plot with H. C. Brown's σ^+-values had a slope of -2.2. This may explain the observation that peroxycarbamates bearing *p*-methyl or *p*-methoxyl groups could not be isolated.

In a previous paper[3] the first-order thermal decompositions of *t*-butyl and cumyl N-phenylperoxycarbamates and *t*-butyl N-α-naphthylperoxycarbamate and their efficiencies as initiators of vinyl polymerization were reported. While *t*-butyl N-α-naphthylperoxycarbamate decomposed more rapidly than the N-phenyl analog, the induced decomposition of the former made an exact comparison difficult. In the present work the effect of substituents in the aromatic rings of *t*-butyl N-phenylperoxycarbamates on their thermal decompositions in toluene has been studied over a 30° range.

[1] Part of this work was supported by the Office of Naval Research under Contract N6onr-26309. Reproduction in whole or in part is permitted for any purpose by the U. S. Government.

[2] This paper is taken from the doctoral dissertation by Eugene L. O'Brien, 1959.

[3] Preceding paper, E. L. O'Brien, F. M. Beringer and R. B. Mesrobian, THIS JOURNAL, **79**, 6238 (1957).

[4] To whom inquiries concerning this paper should be sent: Central Research and Engineering Division, Continental Can Co., Inc., 7622 South Racine Ave., Chicago 20, Ill.

Experimental[5]

Starting Materials.—Liquid isocyanates obtained from Distillation Products, Inc., were redistilled as follows: phenyl, b.p. 55–60° (2 mm.); *m*-tolyl, b.p. 75–76° (10 mm.); *o*-chlorophenyl, b.p. 76–78° (10 mm.); *m*-chlorophenyl, b.p. 76–78° (10 mm.); 2,5-dichlorophenyl, b.p. 118–119° (18 mm.). Solid isocyanates were recrystallized from 28–38° petroleum ether: *p*-bromophenyl, m.p. 41–42°; *p*-chlorophenyl, m.p. 29–30°; *m*-nitrophenyl, m.p. 52–54°; *p*-nitrophenyl, m.p. 53°.

t-Butyl hydroperoxide was purified as previously described.[3] Methanol from Distillation Products, Inc., was of spectro grade. Thiophene-free toluene was distilled from sodium and kept under nitrogen.

Peroxycarbamates.[3,6]—One-tenth mole each of *t*-butyl hydroperoxide and of isocyanate and a few drops of pyridine were dissolved in benzene kept below 30°. After reaction was complete, often in 15 minutes, benzene was removed under reduced pressure, and the residue was crystallized from 28-38° petroleum ether; see Table I.

TABLE I

SUBSTITUTED *t*-BUTYL N-PHENYLPEROXYCARBAMATES

Subst.	M.p. (dec.), °C.	Nitrogen, % Calcd.	Nitrogen, % Found
H	83	6.69	6.64
m-CH_3	54–57	6.28	6.07
o-Cl	71	5.76	6.06
m-Cl	78–79	5.76	6.05
p-Cl	71–72	5.76	5.92
2,5-Cl_2	46–47	5.02	5.25
p-Br	82–84	4.86	5.07
m-NO_2	80	11.02	10.74
p-NO_2	93–94	11.02	10.88

Absorption Spectra.—The infrared spectra were taken of 0.3% mixtures of the peroxycarbamates in potassium bromide disks (300 mg.) with a Perkin–Elmer recording infrared spectrophotometer, using a sodium chloride prism and a speed of one minute/micron. The ultraviolet spectra were taken with a Beckman spectrophotometer, a hydrogen lamp and a slit width of 0.5 mm.

Experimental Results

Rate Data.—The thermal decomposition of the peroxycarbamates in toluene was performed as previously described.[3] The rate data are collected in Table II, and the Eyring activation parameters are given in Table III. Calculations were by the method of least squares.

TABLE II

FIRST-ORDER CONSTANTS FOR THE DECOMPOSITION OF SUBSTITUTED *t*-BUTYL N-PHENYLPEROXYCARBAMATES IN TOLUENE

Subst.	*T*, °C.	$(Concn.)_0$, mmoles liter	10^5k_d sec.$^{-1}$	Subst.	*T*, °C.	$(Concn.)_0$, mmoles liter	10^5k_d, sec.$^{-1}$
H	51.2	1.22	0.34	*p*-Cl	73.0	7.60	5.57
	67.7	6.00	2.31		78.5	8.36	14.2
		6.46	2.31		87.0	7.92	27.5
		7.70	2.32		92.5	10.04	53.7
		32.0	2.31	2,5-Cl_2	88.0	5.00	2.75
	77.7	6.00	11.5		95.0	8.36	5.58
	90.7	10.1	64.1		103.3	10.12	14.8
m-CH_3	64.0	9.74	4.58		114.5	8.96	48.2
	70.7	9.40	9.17	*p*-Br	70.8	4.66	3.32
	78.0	10.7	20.3		79.8	7.10	10.4
	88.5	13.2	57.8		84.0	8.92	17.5
o-Cl	87.0	9.34	3.50		96.0	7.94	77.0
	95.5	10.4	14.8	*m*-NO_2	78.0	9.24	0.84
	103.3	9.40	33.0		88.7	9.12	2.43
m-Cl	78.0	10.92	2.6		98.0	9.88	10.1
	87.0	11.00	7.8		106.0	9.96	23.6
	96.6	8.72	20.3	*p*-NO_2	73.0	7.50	0.64
	102.7	8.66	46.2		87.0	6.76	3.11
					98.0	6.90	8.75
					106.0	6.82	23.8

TABLE III

ACTIVATION PARAMETERS FOR THE DECOMPOSITION OF SUBSTITUTED *t*-BUTYL N-PHENYLPEROXYCARBAMATES IN TOLUENE

Subst.	$\Delta H^{\ddagger}$, kcal./mole	$\Delta S^{\ddagger}$, e.u.	$\Delta F^{\ddagger}$, kcal./mole	log *A*, sec.$^{-1}$
m-CH_3	24.6	−5.9	26.7	11.6
p-NO_2	27.2	−4.2	28.7	11.9
m-Cl	27.6	−1.7	28.2	12.7
p-Cl	28.6	4.0	27.2	13.8
p-Br	30.5	9.4	27.2	14.8
2,5-Cl_2	30.8	5.4	28.9	13.9
m-NO_2	31.8	8.2	28.9	14.5
H	33.4	17.5	27.2	16.7
o-Cl	37.6	25.8	28.5	18.3

The data in Table III show the frequently observed[7] parallel changes of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$.

The Hammett σ–ρ Relationship.—The utility of Hammett's equation[8] for relating rate constants to substituent constants (σ) and for determining reaction constants (ρ) has been shown in free radical decompositions.[9] Recently Brown and co-workers have introduced a new set of substituent constants (σ^+) to correlate better reactions involving electron-deficient intermediates in the rate-determining steps (including electrophilic attack on the benzene ring).[10] For the analysis of the data in Table I, log (k/k_0) is plotted against σ in Fig. 1 and against σ^+ in Fig. 2. The relevant data are collected in Table IV.

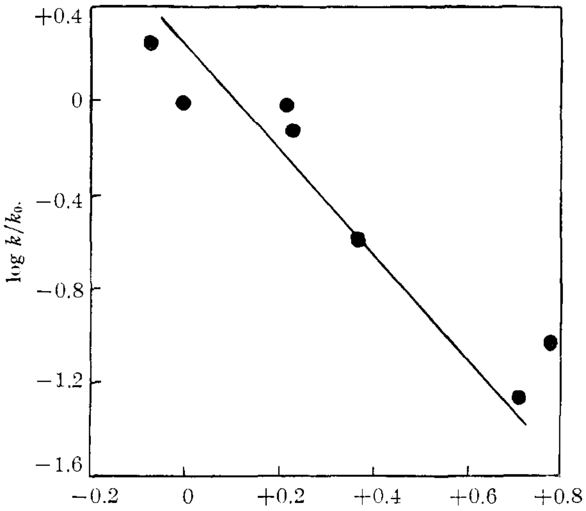


Fig. 1.—The effect of substitution on the decomposition rates of *t*-butyl N-phenylperoxycarbamates using Hammett's σ-values.

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(5) Combustion analyses for nitrogen were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

(6) A. G. Davis and K. H. Hunter, *J. Chem. Soc.*, 1808 (1953).

(7) See J. E. Leffler, *J. Org. Chem.*, **20**, 1203 (1955).

(8) L. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1904, Ch. VII.

(9) Benzoyl peroxides: C. G. Swain, W. T. Stockmayer and J. T. Clarke, THIS JOURNAL, **72**, 4526 (1950); A. T. Blomquist and A. J. Buselli, *ibid.*, **73**, 3883 (1951); *t*-butyl perbenzoates: A. T. Blomquist and I. A. Berstein, *ibid.*, **73**, 5546 (1951); **73**, 3408, 3412, 5546 (1951).

(10) See, for example, H. C. Brown and Y. Okamoto, *ibid.*, **79**, 1913 (1957).

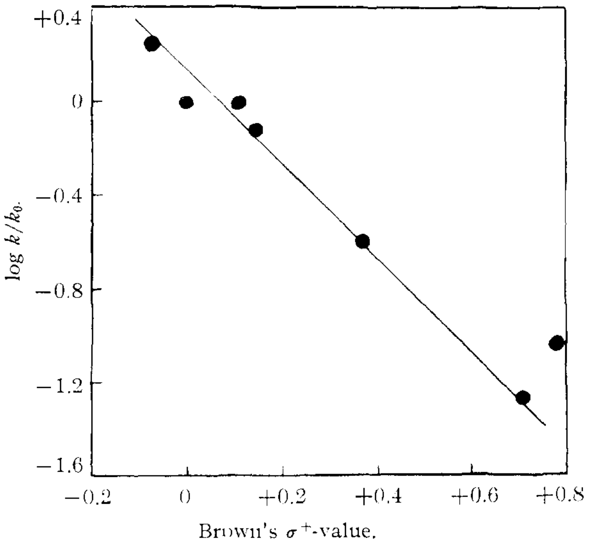


Fig. 2.—The effect of substitution on the decomposition rates of *t*-butyl N-phenylperoxycarbamates using Brown's σ^+-values.

With the Hammett σ-values, ρ at 60, 70, 80 and 90° was found to be −2.21, −2.22, −2.12 and −2.17, while with the Brown σ^+ values ρ was found to be −2.16, −2.16, −2.10 and −2.21.

TABLE IV

EFFECT OF SUBSTITUENTS ON THE RELATIVE RATES OF DECOMPOSITION OF *t*-BUTYL N-PHENYLPEROXYCARBAMATES

Subst.	σ	σ^+	$\log(k/k_0)$ 60°	70°	80°	90°
m-CH_3	−0.069	−0.069	0.584	0.418	0.248	0.111
p-Cl	.226	.112	.226	.076	− .015	− .086
p-Br	.232	.148	− .015	.004	− .126	− .052
m-Cl	.373	.373	− .366	− .475	− .590	− .686
p-NO_2	.778	.778	− .745	− .928	−1.038	−1.146
m-NO_2	.710	.662	−1.181	−1.211	−1.245	−1.268

Absorption Spectra.—An attempt was made to investigate electronic interactions in the substituted *t*-butyl N-phenylperoxycarbamates by determining the position of infrared absorption bands associated with the N–H and C=O groups and by determining the position and intensity of ultraviolet absorption (220–250 mμ) associated with the benzene ring; see Table V.

TABLE V

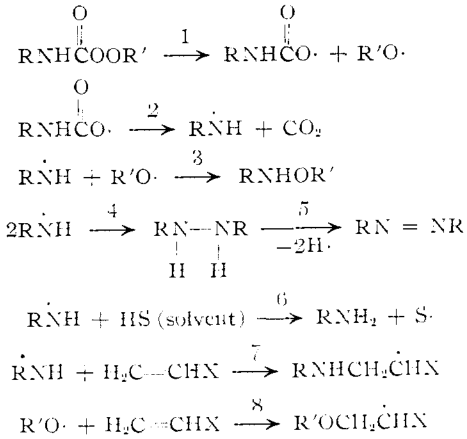
SOME INFRARED AND ULTRAVIOLET ABSORPTION BONDS OF SUBSTITUTED *t*-BUTYL N-PHENYLPEROXYCARBAMATES

Subst.	Infrared C=O μ	N—H μ	Ultraviolet λ_{max}, mμ	ϵ_{max}
2,5-Cl_2	5.69	2.97	236	12,040
p-NO_2	5.74	2.97	220[a]	11,910
m-NO_2	5.77	2.98	234[b]	25,280
p-Br	5.77	3.07	242–243	15,690
p-Cl	5.78	3.08	239–240	20,260
m-Cl	5.81	3.02	236	17,080
m-CH_3	5.81	3.04	234–236	12,830
H	5.81	3.09	233	13,200
o-Cl	5.85	3.02	236	12,040

[a] Also a band at 309 mμ (ϵ_{max} 13,230). [b] Also a band at 268 mμ (ϵ_{max} 13,100).

Discussion

It seems probable that the reactions given represent the decomposition of *t*-butyl peroxycarbamates in the solid state, in solution or in presence of vinyl monomers.



$$RNH\overset{\overset{O}{\|}}{C}OOR' \xrightarrow{1} RNH\overset{\overset{O}{\|}}{C}O\cdot + R'O\cdot$$

$$RNH\overset{\overset{O}{\|}}{C}O\cdot \xrightarrow{2} R\dot{N}H + CO_2$$

$$R\dot{N}H + R'O\cdot \xrightarrow{3} RNHOR'$$

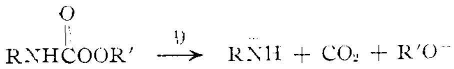
$$2R\dot{N}H \xrightarrow{4} \underset{\underset{H}{|}}{RN}-\underset{\underset{H}{|}}{NR} \xrightarrow[-2H\cdot]{5} RN=NR$$

$$R\dot{N}H + HS\,(\text{solvent}) \xrightarrow{6} RNH_2 + S\cdot$$

$$R\dot{N}H + H_2C=CHX \xrightarrow{7} RNHCH_2\dot{C}HX$$

$$R'O\cdot + H_2C=CHX \xrightarrow{8} R'OCH_2\dot{C}HX$$

In the previous paper[3] by the present authors the formation of carbon dioxide, hydrazo (RNHNHR) and azo (RN=NR) compounds was reported to result from heating *t*-butyl peroxycarbamates in the absence of other materials.[11] *t*-Butyl N-(4-nitrophenyl)-peroxycarbamate has recently been shown by Pedersen[12] to give a substantial amount of O-*t*-butyl-N-(4-nitrophenyl)-hydroxylamine (RNHOR′) on decomposition on the solid state, while the same compound in cumene or ethylbenzene gave large amounts of 4-nitroaniline (RNH_2). These observations, taken with the calculated efficiency of *t*-butyl N-phenylperoxycarbamate in the polymerization of styrene[3] (95%, on the assumption that two initiating fragments are formed per mole of peroxycarbamate), make it probable that the primary step here, as with most other peroxides, is the homolytic scission of the oxygen–oxygen bond, accompanied or followed by loss of carbon dioxide. An alternate mode of decomposition (step 9) to give an aniline cation, carbon dioxide and an alkoxide ion would not be expected to give RNH_2, RNHNHR or RN=NR and would have a lower initiation efficiency toward styrene, as the *t*-butoxide ion would not be effective.



$$RNH\overset{\overset{O}{\|}}{C}OOR' \xrightarrow{9} R\overset{+}{N}H + CO_2 + R'O^-$$

The observation[3] that polystyrene formed by initiation with *t*-butyl N-phenylperoxycarbamate gave an infrared spectrum with a N—H stretching peak but with no C=O absorption indicates that carbon dioxide is lost simultaneously with the peroxide cleavage or that decarboxylation of the carbamate free radical occurs much more rapidly than its addition to styrene.

The change in the rate of decomposition on introducing a nuclear substituent into benzoyl

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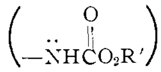
(11) Azo compounds are formed in 25–50% yields by the analogous treatment of isocyanates with hydrogen peroxide and the decomposition of the resulting dicarbamyl peroxides: H. Esser, K. Rastadter and G. Reuter, *Chem. Ber.*, **89**, 685 (1956).

(12) C. J. Pedersen, *J. Org. Chem.*, **23**, 252, 255 (1958).

peroxide or *t*-butyl perbenzoate has been attributed to inductive effects.[9] In both cases the products, benzoate or phenyl radicals, are not significantly stabilized by resonance involving the ring, and the Hammett equation gives a low negative ρ-value (*e.g.*, for benzoyl peroxide, ρ is -0.38). More recently Bartlett and Hiatt[13] have shown that one driving force for the decomposition of peresters is the resonance stabilization of the free radical formed.

In the case of unsubstituted *t*-butyl N-phenylperoxycarbamates the decomposition is most probably controlled by resonance stabilization. Pedersen[12] has reported that *t*-butyl N-ethylperoxycarbamate is extremely stable. The decomposition of *t*-butyl N-α-napthylperoxycarbamate[3] was found in this Laboratory to be very rapid, while the N,N-diphenyl compound was too reactive to be prepared. The stability trend, ethyl > phenyl > α-naphthyl, seems to be that of increased resonance stabilization of the amino radical (not that of inductive control), and supports the picture of loss of carbon dioxide accompanying homolytic peroxide cleavage.[13]

If this scheme is accepted, then the accelerating effect of electron-releasing substituents and the corresponding retarding effect of electron-attracting substituents (ρ is -2.18) can be rationalized on the basis that the imino group $(-\underset{\cdot\cdot}{N}H)$ is much more electronegative than the peroxycarbamido group.



$$\left(-\overset{\cdot\cdot}{N}H\overset{O}{\overset{\|}{C}}O_2R'\right)$$

Electron drift toward the nitrogen, aiding the formation of the anilino radical, would be increased by electron releasing substituents and decreased by electron attracting ones. (Note that in the present work N-*p*-tolyl- and N-p-anisylperoxycarbamates could not be prepared, presumably because of their ease of decomposition.)

In the N-*p*-nitroanilino radical the nitro group is apparently exerting two opposing effects. The polar effect, of withdrawing electrons from the ring, destabilizes the radical. However, as the nitro group can also bear the odd electron, there is added some small resonance stabilization. The result of these effects on the rates of decomposition of ring-substituted *t*-butyl N-phenylperoxycarbamates is: unsubstituted > *p*-nitro > *m*-nitro. On the Hammett plots (Figs. 1 and 2), the *p*-nitro compound is above the line, *i.e.*, it decomposes faster than predicted from the rates of other compounds in which the substituent cannot bear the odd-electron.

The present data are not sufficient for a complete separation of resonance, inductive and steric effects.

BROOKLYN 1, N. Y.

[13] P. D. Bartlett and R. R. Hiatt, THIS JOURNAL, **80**, 1398 (1958).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE PENNSYLVANIA STATE UNIVERSITY]

Bis-(β-diketones). IV. dissociation Constants of Some Bis-(β-diketones)

BY DEAN F. MARTIN[1] AND W. CONARD FERNELIUS

RECEIVED SEPTEMBER 22, 1958

The acid dissociation constants of five bis-(β-diketones) of the type $RCOCH_2CO$–Y–$COCH_2COR$ in a mixed solvent of 75 volume per cent. dioxane and 25 volume per cent. water were measured (or estimated). The fifteen bis-(β-diketones) of the types $[(RCO)(R'CO)CH]_2CHR''$ and $(RCO)(R'CO)CH$-Y-$CH(COR)(COR')$ are so much weaker acids that it was necessary to determine their constants in a more polar enivronment of 50 volume per cent. dioxane and 50 volume per cent. water to keep the titration curve within the range of a *p*H meter. Some correlations of the *pK*D values and structural features of the bis-(β-diketones) are presented.

Introduction

In continuation of a study of the synthesis and properties of bis-(β-diketones)[2–5] the acid dissociation constants of a number of bis-(β-diketones) have been determined. Although several investigations have been concerned with the determination of the dissociation constants of β diketones,[6–10] there seems to be but one study of bis-(β-diketones)[2] which reports the dissociation constants of several compounds of the type $RCOCH_2CO$-Y-$COCH_2COR$. There are reported here the dissociation constants of representative bis-(β-diketones) of the types $RCOCH_2CO$–Y–$COCH_2COR$, $[(RCO)(R'CO)CH]_2CHR''$ and $(RCO)(R'CO)CH$-Y-$CH(COR)(COR')$.

Experimental

Potentiometric Titrations.—The synthesis and properties of the bis-(β-diketones) used in this investigation are described elsewhere.[3–5]

The acid dissociation constants of the bis-(β-diketones) in water–dioxane mixtures containing 75 or 50 volumes per cent. dioxane at 30° were determined by a method described previously[7] using tetramethylammonium hydroxide at the base. Due to the closeness of the first and second

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[1] Department of Chemistry, University College, London.

[2] E. H. Holst, Doctoral Dissertation, The Pennsylvania State University, Aug., 1955.

[3] D. F. Martin, M. Shamma and W. C. Fernelius, THIS JOURNAL, **80**, 4891 (1958).

[4] D. F. Martin, M. Shamma and W. C. Fernelius, *ibid.*, **80**, 5851 (1958).

[5] D. F. Martin, W. C. Fernelius and M. Shamma, *ibid.*, **81**, 130 (1959).

[6] M. Calvin and K. W. Wilson, *ibid.*, **67**, 2003 (1945).

[7] L. G. Van Uitert, *et al.*, *ibid.*, **75**, 451, 455 (1953); **76**, 5887 (1954).

[8] R. M. Izatt, *et al.*, *J. Phys. Chem.*, **58**, 1113 (1954); **59**, 80, 170, 235 (1955).

[9] D. M. Ericson and W. C. Fernelius, AEC Document, NYO-7711, May, 1956.

[10] W. G. Bordiun and G. S. Hammond, "Substituent Effects on the Spectra and Ionization Constants of Diaroylmethanes," U. S. Atomic Energy Commission, Oak Ridge, Tenn., (1954).