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Substituent Effects on the Decarboxylation of Dinitrobenzoate Ions, Representative Aromatic S_E1 Reactions[1]

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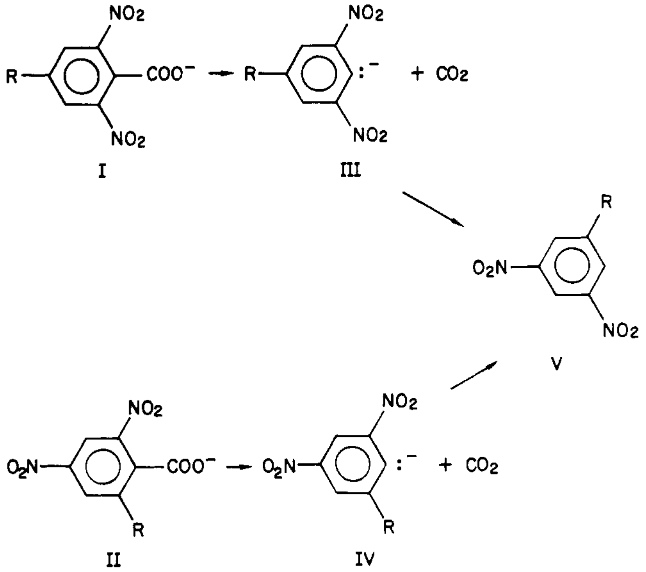
Kinetics of decarboxylation, in water solution, of several 4-substituted 2,6-dinitrobenzoic and 2-substituted 4,6-dinitrobenzoic acids were determined, at several temperatures. The reactions are first order at the low concentrations employed, at which the acids are fully dissociated. Decarboxylation is accelerated by electron-attracting substituents; the Hammett ρ for the effects of 4-substituents is about +2.6. All the decarboxylations involve large positive enthalpies and entropies of activation. The solvent kinetic isotope effect (D_2O/H_2O) is not significantly different from unity. The data support a mechanism wherein the substituted benzoate ion loses CO_2 in the rate-determining step, forming a substituted aryl anion, which is then rapidly hydronated by the solvent. In the case of 2-methoxy-4,6-dinitrobenzoate ion, reaction occurred with strikingly different activation parameters.

S_E1 reactions may be thought of as counterpoint to those that occur by the familiar S_N1 mechanism. Whereas S_N1 reactions occur via carbocation intermediates, S_E1 reactions are characterized by the intermediacy of carbanions.

Although several aromatic S_E1 reactions are known, they are often ignored in broad discussions of aromatic electrophilic substitutions.[3] They have received little attention with regard to substituent effects on reaction rates, in contrast to the abundant attention to their "rich cousins", the aromatic electrophilic substitutions that occur via σ-adduct intermediates. Heretofore, most of the quantitative data have concerned substituent effects on base-catalyzed hydrogen isotope exchange[4-9] and on base-promoted hydrodesilylation.[10] As noted below, the data on these processes are not fully satisfying as evidence for substituent effects.

Attention is called to kinetic measurements on the hydrodehalogenation of several substituted aryl halides by solutions of bases in carbanion-yielding solvents such as 2-butanone and dimethyl sulfoxide conducted by Bolton and co-workers.[11-13] The mechanism is believed to be one of nucleophilic capture of halogen by a carbanion derived from the solvent, furnishing an aryl anion intermediate, which is then hydronated[14] by the solvent.[15] Acceleration by halogen and trifluoromethyl groups, most strongly ortho, most weakly para, was demonstrated.

Scheme I. Postulated Mechanism for the Thermal Decarboxylation of Carboxylate Ions of Types I and II in Dilute Aqueous Solution[a]



[a] b, R = Br; c, R = Cl; h, R = H; i, R = I; n, R = NO_2; o, R = OMe.

There have also been qualitative indications of aromatic S_E1 substituent effects. Thus, nitro and halogen substituents, especially in the ortho position, have been observed to facilitate the cleavage or hydrodeformylation of benzaldehydes by bases, as in the cleavage of 2,6-dichlorobenzaldehyde to formate ion and *m*-dichlorobenzene by aqueous hydroxide ion.[16,17] Similarly, *o*-halobenzophenones but not their meta or para isomers nor benzophenone itself are rapidly cleaved by KNH_2 in ammonia.[18]

As a means of getting further information about substituent effects on reactions via aryl anion intermediates, we undertook a study of the hydrodecarboxylation of substituted dinitrobenzoate ions in aqueous solution. We chose to examine two series: 4-substituted 2,6-dinitrobenzoate and 2-substituted 4,6-dinitrobenzoate ions.

It has long been known that 2,4,6-trinitrobenzoic acid undergoes facile decarboxylation in water. An early study

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(3) Mach, M. H.; Bunnett, J. F. *J. Am. Chem. Soc.* **1974**, *96*, 936.

(4) Shatenshtein, A. I. *Tetrahedron* **1962**, *18*, 95; *Adv. Phys. Org. Chem.* **1963**, *1*, 156.

(5) Hall, G. E.; Piccolini, R.; Roberts, J. D. *J. Am. Chem. Soc.* **1955**, *77*, 4540.

(6) Hall, G. E.; Libby, E. M.; James, E. L. *J. Org. Chem.* **1963**, *28*, 311.

(7) Streitwieser, A., Jr.; Mares, F. *J. Am. Chem. Soc.* **1968**, *90*, 644.

(8) Streitwieser, A., Jr.; Hudson, J. A.; Mares F. *J. Am. Chem. Soc.* **1968**, *90*, 648.

(9) Streitwieser, A., Jr.; Scannon, P. J.; Niemeyer, H. M. *J. Am. Chem. Soc.* **1972**, *94*, 7936.

(10) Seconi, G.; Taddei, M.; Eaborn, C.; Stamper, J. G. *J. Chem. Soc., Perkin Trans. 2* **1982**, 643.

(11) Bolton, R.: Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1976**, 1545.

(12) Bolton, R.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1977**, 278.

(13) Bolton, R.; Moore, C.; Sandall, J. P. B. *J. Chem. Soc., Perkin Trans. 2* **1982**, 1593.

(14) "Hydron" is a term for a monohydrogen cation of charge +1. Hydrons comprise protons, deuterons, and tritons.

(15) Bunnett, J. F.; Victor, R. R. *J. Am. Chem. Soc.* **1968**, *90*, 810.

(16) Lock, G. *Ber. Deutsch. Chem. Ges.* **1936**, *69B*, 2253 and earlier papers.

(17) Bunnett, J. F.; Miles, J. H.; Nahabedian, K. V. *J. Am. Chem. Soc.* **1961**, *83*, 2512.

(18) Bunnett, J. F.; Hrutfiord, B. F. *J. Org. Chem.* **1962**, *27*, 4152.

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by Moelwyn-Hughes and Hinshelwood[19] demonstrated that the reaction occurs at measurable rate in the temperature range 70–100 °C and that the activation enthalpy and entropy are both quite high.

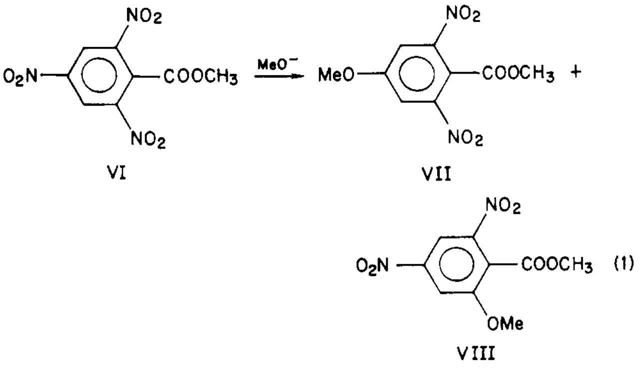
Kinetic studies by Verhoek[20] indicated that the reaction in ethanol is first order in the 2,4,6-trinitrobenzoate ion; he proposed decomposition of that ion to be the rate-determining step. His study showed the reaction rate to be higher and the enthalpy and entropy of activation to be lower in ethanol than in water. He suggested that the ion is more stable in water because of higher solvation than in alcohol and that "decomposition when it does occur involves a greater energy of desolvation". Trivich and Verhoek[21] determined the reaction rate in water–dioxane mixtures; the rate increased with increasing dioxane content in the solvent, and the activation enthalpy decreased concurrently.

Riesz and Bigeleisen[22] observed $^{12}C/^{13}C$ kinetic isotope effects on the decarboxylation of the 2,4,6-trinitrobenzoate ion of natural isotopic abundance in water and in 90% ethanol/10% water solvents. k_{12}/k_{13} was about 1.035. This is consistent with rate-determining scission of the bond between the carboxyl carbon and C-1 of the aromatic ring to form CO_2 and the 2,4,6-trinitrophenyl anion. The entropy of activation was reckoned as +25 eu in water and +12 eu in 100% ethanol;[22] this was taken as "indicative of the fact that the ground state is the more highly solvated".

Thus, all the evidence suggests the mechanism of Scheme I for the decarboxylation reactions we chose to study.

Results

Synthesis of Substrates. Most of the desired dinitrobenzoic acid derivatives, although previously unknown, were accessible by chromic acid oxidation of the corresponding substituted toluenes. However, oxidation of 4-methoxy-2,6-dinitrotoluene was unsatisfactory. Accordingly, acid Io was obtained by an alternative approach, namely, the reaction of sodium methoxide with methyl 2,4,6-trinitrobenzoate (VI) to effect methoxydenitration (eq 1). Replacement of both *o*- and *p*-nitro groups occurred, but principally the para; also, inasmuch as VII was less soluble than VIII, it could be obtained in moderately good yield (54%).



Kinetics. Kinetic studies of the decarboxylation reactions were conducted in aqueous solution with the substrate approximately 10^{-4} M. From the reported pK_a value (1.42)[23] for IIh, very nearly the weakest acid involved in our work, one deduces that at this low concentration it is fully dissociated. We verified by pH measurement that each substituted dinitrobenzoic acid was fully dissociated at the stated concentration level. Accordingly, no base was added to convert the acid to its anion, nor was any salt or other solute present. Inasmuch as the vis–UV spectrum of each substrate at this concentration level differed from that of the "infinity" solution at the end of a kinetic run, it was possible to follow the progress of all reactions by absorbance measurements. Clean first-order kinetic behavior was observed without exception.

Table I. First-Order Rate Constants (×10^4) for Decarboxylation of 4-Substituted 2,6-Dinitrobenzoic Acids in Water Solution

temp, °C	4-substituent					
	NO_2	Br	Cl	I	H	OMe
89.7	2.22					
99.5					0.0239	
99.6	8.01					
	8.08					
100.1			0.29			
			0.291			
100.4				0.334	0.0286	
100.7				0.267		
101		0.339				
		0.357				
106.5	20.84					
	21.01					
111			1.337			
111.2	37.7					
111.4		1.423		1.233	0.1442	
120.6		5.04	5.01	4.2		
120.7					0.534	
(125.0)[a]	193	8.99	8.81	7.04	0.913	0.586
126.6						0.715
						0.815
133		24.9	25.6			
		25.1	25.9			
133.1					2.53	
133.2						1.75
133.4					2.71	
133.5				18.6		
				18.8		
143.5						6.69
149.3						12.85
						13.46

[a] Interpolated or extrapolated rate constants.

One substrate, namely, 2-methoxy-4,6-dinitrobenzoic acid (IIo) behaved anomalously. No 3,5-dinitroanisole could be isolated as a product; the product that was tangible had TLC R_f values suggestive of 2-hydroxy-4,6-dinitrobenzoic acid. As noted below, this reaction showed activation parameters quite different from the rest.

The rate constants determined for decarboxylation of the 4-substituted 2,6-dinitrobenzoate ions are displayed in Table I. Corresponding data for the 2-substituted 4,6-dinitrobenzoate ions (including the anomalous IIo) appear in Table II. Enthalpies and entropies of activation were calculated for all decarboxylations; they are listed in Table III.

Solvent Isotope Effect. The decarboxylation of In was determined in both normal water and in deuterium oxide solution, in experiments carefully arranged to provide exactly the same conditions for the two solvent systems. Such matched determinations were conducted at 65, 75,

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[19] Moelwyn-Hughes, E. A.; Hinshelwood, C. N. *Proc. R. Soc. London, Ser. A* **1931**, *131*, 186. See also: Johnson, P.; Moelwyn-Hughes, E. A. *Ibid.* **1940**, *175*, 118; Moelwyn-Hughes, E. A. "The Chemical Statics and Kinetics of Solutions"; Academic Press: New York, 1971; p 305.

[20] Verhoek, F. H. *J. Am. Chem. Soc.* **1939**, *61*, 186.

[21] Trivich, D.; Verhoek, F. H. *J. Am. Chem. Soc.* **1943**, *65*, 1919.

[22] Riesz, P.; Bigeleisen, J. *J. Am. Chem. Soc.* **1959**, *81*, 6187.

[23] Kortum, G.; Vogel, W.; Andrussow, K. "Dissociation Constants of Organic Acids in Aqueous Solution"; Butterworths: London, 1961; p 378.

Table II. First-Order Rate Constants ($\times 10^5$) for Decarboxylation of 2-Substituted 4,6-Dinitrobenzoic Acids in Water Solution

temp, °C	2-substituent					
	NO_2	Br	Cl	I	H	OMe
89.7	22.2					
99.6	80.1					
	80.8					
106.5	208.4					
	210.1					
111.2	377					
117.6		0.776				
125.2		2.54				
125.6			1.92	0.813		
127.7						14.85
133.3		8.24	5.24			
133.6				2.71		
134.1				2.76		
134.3						24.3
143.4		30				
143.6			22.4	8.31		49.5
149.3			46.8			
149.4				18.8		
149.8						75
172.5					0.512	
190					3.76	
205					19.4	
210					29.5	

Table III. Activation Parameters for Decarboxylation Reactions

	series I		series II	
	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}	$\Delta H^{\ddagger}$, kcal mol^{-1}	$\Delta S^{\ddagger}$, cal deg^{-1} mol^{-1}
NO_2	35.6 ± 0.5	23	35.6 ± 0.5	22
Br	39.4 ± 0.4	26	44.7 ± 0.7	32
Cl	39.6 ± 0.1	26.5 ± 0.3	45	32
I	38.8 ± 0.4	24	42	24
H	41.0 ± 0.3	25.4 ± 0.8	46	19
OMe	42.2 ± 0.05	27		

and 82 °C. No significant difference in rate constants between the two solvents could be observed. Our best estimate of k_H/k_D is 1.026 ± 0.054; inasmuch as it differs from unity by less than the root variance of the measurements, this estimate is not significantly different from 1.000. Our data appear in Table IV.

Discussion

Effects of 4-Substituents. Upon gross inspection of the kinetic data in Table I for decarboxylation of substrates of type I (Scheme I), one sees that electron-attracting substituents accelerate the reaction. A plot (not shown) of log k vs. original Hammett σ values[24] approximates a straight line and furnishes an estimate of ρ of +2.6.

Inasmuch as the mechanism of Scheme I involves formation of a high energy intermediate with negative charge on C-1, facilitation by electron-attracting substituents is not surprising. It is, however, noteworthy that the ρ value is considerably less than that for aromatic nucleophilic substitutions by the S_NAr mechanism,[25] for which a ρ of +4 or higher is often observed. The lower sensitivity of the decarboxylations has to do with the location of the negative charge in the respective high energy intermediates. In S_NAr reactions, the σ-adduct intermediate has negative charge delocalized in the π-orbital system, while aryl anion III of Scheme I has its negative charge formally located in a σ-orbital from which it cannot be delocalized onto other ring carbon atoms because of an orthogonality constraint.

Table IV. Kinetics of Decarboxylation of 2,4,6-Trinitrobenoic Acid in Ordinary Water and in Deuterium Oxide

temp, °C		rate constant, s^{-1}			
		H_2O	root var	D_2O	root var
65.0		5.72		5.78	
		6.36		6.64	
				6.44	
	mean	6.04	0.32	6.29	0.37
75.0		27.7		27.4	
		29.1		28.8	
				26.9	
	mean	28.4	0.7	27.7	0.8
82.0		64.6		60	
		67.8		61.2	
				60.5	
	mean	66.2	1.6	60.6	0.5

An alternative correlation, namely, with dehydronation energies of monosubstituted benzenes as calculated by Eaborn, Stamper, and Seconi,[26] gives a better fit. This and other correlations are considered in depth in the accompanying paper.[27]

Effects of 2-Substituents. The kinetic data in Table II, except for the methoxy substrate, pertain to the decarboxylation of 2-substituted 4,6-dinitrobenzoate ions. They show the order of substituent effect on reactivity: $NO_2 \gg Br > Cl > I \gg H$. Qualitatively the substituent effects are similar to those in decarboxylation of substrates of type I.

Scrutiny of these data by correlation analysis requires utilization of the appropriate substituent parameter(s). That is a matter of some subtlety which is dealt with in the accompanying paper.[27]

Activation Parameters. Enthalpies and entropies of activation calculated straightforwardly from kinetic data in Tables I and II for decarboxylation reactions are displayed in Table III. It is noteworthy, as observed earlier for decarboxylation of 2,4,6-trinitrobenzoate ion,[19-22] that the activation enthalpy is high and that the activation entropy is large and positive. In contrast, for the exceptional reaction of IIo, the activation enthalpy is 24.0 kcal mol^{-1} and the entropy of activation is −17 cal deg^{-1} mol^{-1}.

Reaction Mechanism. The data presented are compatible with the reaction mechanism sketched in Scheme I. We have commented that the substituent effects are consistent with development of negative charge in a σ-orbital (sp^2) in the rate-limiting transition state, which lies between I and III or between II and IV. The ionic carboxylate group in I or II surely is strongly solvated. Inasmuch as considerably less charge resides in the CO_2 moiety in the transition state, much of that solvation must be released, at enthalpic cost. The release of solvation increases the entropy of the transition state. In ethanol, solvation of the carboxylate group in the substrate is lower, and therefore there is less change in enthalpy or entropy in forming the transition state.[22]

A conceivable alternative to the mechanism of Scheme I would have a water molecule hydronate C-1 as CO_2 separated and thus avoid formation of the high energy carbanion as an actual intermediate. The fact that there is no solvent isotope effect disqualifies this alternative.[28,29]

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[24] Hammett, L. P. "Physical Organic Chemistry", 2nd ed.; McGraw-Hill: New York, 1970; p 356.

[25] Bunnett, J. F. *Q. Rev. Chem. Soc.* **1958**, *12*, 1.

[26] Eaborn, C.; Stamper, J. G.; Seconi, G. *J. Organomet. Chem.* **1981**, *204*, 27.

[27] Segura, P. *J. Org. Chem.*, following paper in this issue.

[28] Schowen, R. L. *Progr. Phys. Org. Chem.* **1972**, *9*, 275.

Also, it may be noted that this alternative would involve less increase in enthalpy and entropy on forming the transition state and thus would be less compatible with the observed high enthalpies and entropies of activation.

We consider the data we have obtained to be more reliable as evidence of substituent effects on the formation of aryl anions than the previously mentioned measurements on rates of hydrogen isotope exchange with KNH_2 in ammonia[4] and on rates of base-promoted hydrodesilylation.[10] The chief difficulty with the earlier data is that for neither series of reactions was the rate law well defined. Also, the precision of the hydrogen isotope exchange rate data is low: only one or two significant figures.

Scrutiny of Substituent Effects. The data we have obtained reveal much about the nature of substituent effects in the systems studied. A searching analysis of them is reported in the accompanying paper.[27]

Experimental Section

Synthesis of Substituted Toluenes. 2-Bromo-4,6-dinitrotoluene, mp 55–57 °C, and 4-bromo-2,6-dinitrotoluene, mp 86–87 °C, were made by bromination of the respective dinitrotoluenes with the method of Derbyshire and Waters.[30] 2-Iodo-4,6-dinitrotoluene, mp 81–82 °C, and 4-iodo-2,6-dinitrotoluene, mp 88–90 °C, were prepared by iodination of the respective dinitrotoluenes with the method of Arotsky and Butler.[31] 2-Methoxy-4,6-dinitrotoluene was obtained in 91% yield by methylation of the corresponding phenol by a procedure similar to that described by Pailer and Bergthaller.[32]

2-Chloro-4,6-dinitrotoluene. 2,4-Dinitrotoluene (18 g, 0.10 mol) was added to a solution of 16 g of silver sulfate in concentrated sulfuric acid (100 mL) and water (14 mL). After 10 min of stirring at room temperature, the mixture was heated to ca. 85 °C, and chlorine gas was bubbled through it with constant stirring for 40 h. The reaction mixture was cooled and poured onto crushed ice; after filtration, the filtrate was extracted with dichloromethane. Evaporation of the extract left an oily residue (19 g), the ^{1}H NMR spectrum of which indicated it to comprise about 90% the desired chloro compound, the rest being the starting material. The oily material was used in the ensuing oxidation step.

4-Chloro-2,6-dinitrotoluene. A similar procedure was employed. Ten grams of 2,6-dinitrotoluene, 8.6 g of silver sulfate, 60 mL of sulfuric acid, and 8 mL of water were used, and the duration of chlorination was 8 days at 80–90 °C. The residue from evaporation of the dichloromethane extract was purified by flash chromatography with hexane/chloroform (1/1) being used as eluant. 4-Chloro-2,6-dinitrotoluene, mp 74–75 °C (lit.[33] mp 76 °C) was obtained in the amount of 4.5 g (40%).

Oxidation of Substituted Toluenes to Substituted Benzoic Acids. In all cases the proportions used were 1 mmol of the toluene derivative to 1.35 mmol of sodium dichromate and 1.37 mL of concentrated sulfuric acid. To a stirred mixture of the toluene derivative and sulfuric acid was added the sodium dichromate portionwise over a period of about 1.5 h. The reaction was exothermic; no heating was necessary. The reaction mixture was then poured slowly onto crushed ice. After filtration, the filtrate was extracted for 10 to 15 h with dichloromethane in a continuous extractor. The solid obtained after evaporation of the dichloromethane extract was combined with that collected in the filtration, and the mixed solids were stirred with water under gentle heating while potassium carbonate was added until the mixture was strongly basic. The resulting mixture was filtered, and 50% aqueous sulfuric acid was added in excess; if precipitation did not occur immediately, the solution was concentrated by evaporation until it did occur. The benzoic acid derivative so obtained was recrystallized from water or benzene. All yields are of crude material; all melting points are uncorrected.

2,4-Dinitrobenzoic acid (IIh): mp 182–183 °C (lit.[34] mp 183 °C); IR (cm^{-1}, KBr) 1730 (C=O), 1540 and 1350 (NO_2).

2,6-Dinitrobenzoic acid (Ih): mp 202–203 °C (lit.[34] mp 202–203 °C); IR (cm^{-1}, KBr) 2400–3400 (OH), 1730 (C=O), 1550 and 1350 (NO_2).

4-Iodo-2,6-dinitrobenzoic acid (Ii): mp 226–227 °C; IR (cm^{-1}, KBr) 2200–3200 (OH), 1720 (C=O), 1530 and 1340 (NO_2); MS *m/e* (relative intensity, composition) 338 (25, $C_7H_3IN_2O_6$), 294 (63, $C_6H_2IN_2O_4$) 248 (16, $C_6H_2INO_2$), 201 (22, C_6H_2I), 75 (100, C_6H_3), 74 (79, C_6H_2); ^{1}H NMR (Me_2SO-d_6) δ 8.5 (s, Ar-H); UV λ_{max} (water) 222 nm (log ϵ 4.34), 333 (3.28). Anal. Calcd for $C_7H_3IN_2O_6$: C, 24.87; H, 0.90; N, 8.29. Found: C, 24.62; H, 0.80; N, 8.10.

2-Iodo-4,6-dinitrobenzoic acid (IIi): mp 220–221 °C; IR (cm^{-1}, KBr) 2700–3200 (OH), 1720 (C=O), 1525 and 1340 (NO_2); MS, *m/e* (relative intensity, composition) 338 (59, $C_7H_3IN_2O_6$), 294 (34, $C_6H_2IN_2O_4$), 248 (16, $C_6H_3INO_2$), 201 (13, C_6H_2I), 75 (53, C_6H_3), 74 (100, C_6H_2); ^{1}H NMR (Me_2SO-d_6) δ 8.50 (d, 1 H), 8.68 (d, 1 H, J = 2.0 Hz); UV λ_{max} (water) 222 nm (log ϵ 4.25), 260 (4.01). Anal. Calcd for $C_7H_3IN_2O_6$: C, 24.87; H, 0.90; N, 8.29. Found: C, 24.97; H, 0.84; N, 8.37.

4-Bromo-2,6-dinitrobenzoic acid (Ib): mp 215–216 °C; IR (cm^{-1}, KBr) 2400–3200 (OH), 1730 (C=O), 1555 and 1350 (NO_2); MS, *m/e* (relative intensity, composition) 290/292 (12, $C_7H_3BrN_2O_6$), 246/248 (33, $C_6H_3BrN_2O_4$), 200/202 (17, $C_6H_3BrNO_2$), 75 (100, C_6H_3), 74 (83, C_6H_2); ^{1}H NMR (acetone-d_6) δ 8.66 (s, ArH); UV λ_{max} (water) 212 nm (log ϵ 4.30), 244 (4.12). Anal. Calcd for $C_7H_3BrN_2O_6$: C, 28.89; H, 1.04; N, 9.63. Found: C, 28.74; H, 0.99; N, 9.32.

2-Bromo-4,6-dinitrobenzoic acid (IIb): mp 209–210 °C; IR (cm^{-1}, KBr) 2500–3300 (OH), 1740 (C=O), 1545 and 1355 (NO_2); MS, *m/e* (relative intensity, composition) 290/292 (100, $C_7H_3BrN_2O_6$), 246/248 (89, $C_6H_3BrN_2O_4$), 200/202 (38, $C_6H_3BrNO_2$); ^{1}H NMR (acetone-d_6) δ 8.84 (d, 1 H), 8.92 (d, 1 H, J = 3 Hz); UV λ_{max} (water) 204 nm (log ϵ 4.26), 252 (4.13). Anal. Calcd for $C_7H_3BrN_2O_6$: C, 28.89; H, 1.04; N, 9.63. Found: C, 28.68; H, 0.97; N, 9.68.

4-Chloro-2,6-dinitrobenzoic acid (Ic): mp 205–206 °C; IR (cm^{-1}, KBr) 2400–3100 (OH), 1725 (C=O), 1550 and 1350 (NO_2); MS, *m/e* (relative intensity, composition) 202 (93, $C_6H_3ClN_2O_4$), 109 (97, C_6H_2Cl), 75 (100, C_6H_3); ^{1}H NMR (acetone-d_6) δ 8.54 (s, ArH); UV λ_{max} (water) 208 nm (log ϵ 4.32), 243 (4.13). Anal. Calcd for $C_7H_3ClN_2O_6$: C, 34.10; H, 1.23; N, 11.36. Found: C, 34.32; H, 1.51; N, 11.21.

2-Chloro-4,6-dinitrobenzoic acid (IIc): mp 199–200 °C; IR (cm^{-1}, KBr) 2400–3300 (OH), 1725 (C=O), 1525 and 1340 (NO_2); MS *m/e* (relative intensity, composition) 246 (38, $C_7H_3ClN_2O_6$), 202 (28, $C_6H_3ClN_2O_4$), 74 (100, C_6H_2); UV λ_{max} (water) 201 nm (log ϵ 4.26), 249 (4.14). Anal. Calcd for $C_7H_3ClN_2O_6$: C, 34.10; H, 1.23; N, 11.36. Found: C, 34.37; H, 1.13; N, 11.41.

2-Methoxy-4,6-dinitrobenzoic acid (IIo): mp 150–151 °C; IR (cm^{-1}, KBr) 2400–3200 (OH), 1710 (C=O), 1560 and 1350 (NO_2); MS, *m/e* (relative intensity, composition) 242 (0.5, $C_8H_6N_2O_7$), 194 (100, $C_8H_4NO_5$); UV λ_{max} (water) 205 nm (log ϵ 4.19), 245 (shoulder, 3.97). Anal. Calcd for $C_8H_6N_2O_7$: C, 39.68; H, 2.50; N, 11.57. Found: C, 40.01; H, 2.59; N, 11.45. The yield of this acid from oxidation of the corresponding toluene was only 5%; about 20% of an orange solid with physical properties characteristic of 2-hydroxy-4,6-dinitrobenzoic acid was also obtained.

2,4,6-Trinitrobenzoic acid (In) was made according to the procedure in ref. 35.

Reaction of Methyl 2,4,6-Trinitrobenzoate with Sodium Methoxide. A solution of 0.4 g of sodium methoxide in 5 mL of methanol was combined with a solution of 1.9 g of methyl 2,4,6-trinitrobenzoate in 15 mL of methanol, and the mixture was heated at reflux for 30 min. The mixture was diluted with water, neutralized by addition of dilute sulfuric acid, and extracted with methylene chloride. Evaporation of the extract left an oil, the ^{1}H NMR spectrum of which indicated it to contain the methyl esters of 4-methoxy-2,6-dinitro- and 2-methoxy-4,6-dinitrobenzoic

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(29) Melander, L.; Saunders, W. H., Jr. "Reaction Rates of Isotopic Molecules"; Wiley: New York, 1980; Chapter 7.

(30) Derbyshire, D. H.; Waters, W. A. *J. Chem. Soc.* **1950**, 573.

(31) Arotsky, J.; Butler, R. *J. Chem. Soc. C* **1970**, 1480.

(32) Pailer, M.; Bergthaller, P. *Monatsh. Chem.* **1967**, 98, 579.

(33) Parkes, G. D.; Farthing, A. C. *J. Chem. Soc.* **1948**, 1275.

(34) *Beilstein*, 9, **1926**, 411.

(35) Clarke, H. T.; Hartman, W. H. "Organic Syntheses"; Wiley: New York, 1941; Collect Vol. I p 543.

J. Org. Chem. 1985, 50, 1045–1053 1045

acids, in proportions about 5:4, respectively. The oil was dissolved in a small amount of chloroform and, at its boiling point, petroleum ether was added; upon cooling, white crystals of methyl 4-methoxy-2,6-dinitrobenzoate separated: mp 104–105 °C; IR (cm^{-1}, KBr) 1750 (C=O), 1550 and 1350 (NO_2); MS, *m/e* (relative intensity, composition) 256 (11, $C_9H_8N_2O_7$), 225 (100, $C_8H_5N_2O_6$), 179 (11, $C_8H_5NO_4$); ^1H NMR ($CDCl_3$) δ 7.7 (2 H, Ar H), 3.8 (6 H, OMe).

4-Methoxy-2,6-dinitrobenzoic acid (Io) was obtained by saponification of its methyl ester by methanolic sodium hydroxide. The acid was recrystallized from benzene: mp 179–180 °C; IR (cm^{-1}, KBr) 2400–3300 (OH) 1725 (C=O), 1550 and 1350 (NO_2); MS *m/e* (relative intensity, composition) 242 (50, $C_8H_6N_2O_7$), 227 (35, $C_7H_3N_2O_7$), 210 (42, $C_7H_2N_2O_7$), 198 (30, $C_7H_6N_2O_5$), 179 (20, $C_7H_3N_2O_4$), 122 (100, $C_6H_4NO_2$); UV λ_{max} (water) 210 nm (log ϵ 4.32). Anal. Calcd for $C_8H_6N_2O_7$: C, 39.68; H, 2.50; N, 11.57. Found: C, 39.9; H, 2.71; N, 10.98.

Expected Products of Decarboxylation. 5-Iodo-1,3-dinitrobenzene (Vi), mp 101–102 °C, was obtained by iodination of *m*-dinitrobenzene, by following the method of Arotsky and Butler.[31] **1-Bromo-3,5-dinitrobenzene (Vb)**, mp 76–77 °C, was made by bromination of *m*-dinitrobenzene, by following the method of Derbyshire and Waters.[30] **3,5-Dinitroanisole (Vo)** was prepared by the action of sodium methoxide on 1,3,5-trinitrobenzene.[36]

Products of Decarboxylation. Dilute solutions, ca. 1.5 L at concentration of (1–2) × 10^{-4} M, of carboxylic acids of series I and II were heated in sealed vessels at 125 °C for 8–10 decarboxylation half-lives, as determined by kinetic measurements. The cooled contents of the vessels were extracted 5 times with 100-mL portions of methylene chloride. Evaporation of the extracts in each case but two left a residue which was shown by its MS and ^1H NMR spectra and its TLC behavior (MeOH/chloroform, 1/4) to be identical with an authentic sample of the anticipated decarboxylation product. In regard to chloro substrates Ic and IIc, no authentic 1-chloro-3,5-dinitrobenzene was synthesized; the residues after reaction showed spectra characteristics expected of this compound. The product from 2-methoxy-4,6-dinitrobenzoic acid (IIo) was not 3,5-dinitroanisole but rather a solid with TLC R_f similar to the R_f for 2-hydroxy-4,6-dinitrobenzoic acid.

Kinetic Measurements. Each decarboxylation reaction was examined preliminarily by heating portions of an aqueous solution of it, sealed in glass, for varying periods of time at a temperature expected to be conducive to decarboxylation. UV–vis spectra of the resulting solutions were recorded. In every case two significant features were noted: the final spectrum differed significantly from the initial in absorbance at one or more wave lengths and there were well-defined isosbestic points. A wavelength at which absorbance changed significantly during reaction (usually in the range 220–250 nm) was chosen for monitoring of reaction in kinetic runs.

For temperatures up to 150 °C, liquid thermostat baths were used; temperature variation was about ±0.1°. For higher temperatures, a temperature-controlled "bath" of fluidized aluminum oxide, with a variability of ca. ±0.5°, was employed.

Solutions of carboxylic acids in series I and II, ca. 1 × 10^{-4} M in deionized water, were apportioned in 5-mL aliquots into glass ampules which were then sealed. For runs at temperatures up to 150 °C, thin-walled, flat-bottomed ampules such as used to package medicinal drugs were used, but heavy-walled glass ampules were used at higher temperatures. The ampules for a run, usually 15 in number, were placed in the thermostat all at once and single ampules were removed at recorded times, mostly during the first 4 half-lives. Upon removal from the thermostat at less than 150 °C, ampules were immediately plunged into cold water, while ampules removed from the hotter thermostat were placed in a stainless steel beaker and allowed to cool. The absorbance of the solution within each ampule was determined at the chosen wavelength. Plots of ln ($A_t - A_{inf}$) vs. time were linear without exception; for evaluation of first-order rate constants, the negatives of the slopes calculated by a weighted least-squares procedure were taken, the weighting factor being $(A_t - A_{inf})^2$. (A_t is absorbance at time *t* and A_{inf} is the absorbance at "infinity"; for very slow runs, A_{inf} was calculated by use of a computer.)

Enthalpies and entropies of activation were reckoned by means of standard expressions.[37]

Solvent Isotope Effect Experiments. Reaction solutions were prepared in the usual way and placed in standard square cuvettes which were tightly capped but not sealed. Kinetic runs were performed in a Perkin-Elmer 559A spectrophotometer, which has a thermostated cell compartment, a cuvette holder with room for five cuvettes, and records absorbances automatically as programmed. (We thank Prof. C. F. Bernasconi for permission to use this instrument.) During each set of determinations, there were concurrently within the cell compartment two cuvettes with ordinary water and three with deuterium oxide solvent. Reactions were followed for about 2 half-lives. Their rate constants, reckoned from absorbance change in the usual way, are listed in Table IV.

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[36] Reverdin, F. "Organic Syntheses"; Wiley: New York, 1941; Collect. Vol. I, p 219.

[37] Bunnett, J. F. "Investigation of Rates and Mechanisms of Reactions", 3rd ed.; Lewis, E. S., Ed.; Wiley: New York, 1974; p 402.

Simultaneous Use of Empirical and Semiempirical Substituent Parameters as a New Method of Analysis of the Ortho Effect. Application in Reactions via Aryl Anion Intermediates[1]

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A new method to estimate ortho parameters suitable to factor the ordinary electronic effect in the correlation analysis of the ortho effect is described. It is based on calculated MO energies of appropriate isodesmic processes. The superiority of the use of these semiempirical ortho parameters, compared with the current method of Fujita and Nishioka, is illustrated by analysis of the ortho effect in three reactions for which aryl anion intermediates have been postulated. A qualitative theoretical interpretation of the separation between ordinary and proximity electronic effects is given.

The peculiar behavior of ortho-substituted benzene derivatives in chemical reactivity, chemical equilibrium, and other properties, compared with that of the corresponding para- and meta-substituted compounds, is usu-

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