J = 16.0 and 4.5 Hz) (CH_2 at C_6), 6.34 (singlet, OCH_3 of ester), 7.87 (broad doublet with small intensity, J = 2.6 Hz, CH at C_5).

Thermal Isomerization of 3,7-Dideuterio-4-isopropyl-1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (VI). After 200 mg (1.1 mmol) of neat VI was heated at 180° in a sealed tube under nitrogen atmosphere for 135 min, the pyrolysate was dissolved in benzene and the solution was chromatographed on a column containing 10 g of silica gel. The benzene-ether (25:1) fractions afforded 101 mg (51%) of VIII as a yellow oil: bp 95–100° (bath temperature) (1 mm); $\nu_{\max}^{\text{liq}}$ 1705, 1592, 725, and 685 cm^{-1}; m/e 180 (M$^+$); nmr spectrum, see Table II. The ether fractions gave 21 mg (11%) of XII.

Reaction Rate of the Cope Rearrangement of 4-Isopropyl-1-methoxybicyclo[3.2.0]hepta-3,6-dien-2-one (Ib). The material used for this kinetic study was purified by redistillation of the ordinary photoproduct (Ib) described previously using a spinning band column. Vapor phase chromatographic analysis of the distillate, bp 79–80° (1 mm), revealed no evidence of contamination of Ib. The reaction vessel was made of Pyrex tubing, 5 mm o.d. and 60 mm in length, with a thick sphere 6 mm in diameter at the bottom. About 30 mg of the material was introduced into the vessel and it was sealed under a nitrogen stream. Eight reaction tubes and a thermometer were fitted in the necks of a 500-ml flask with nine necks and a reflux condenser, which contained a suitable solvent. Eight vessels were heated at the same time by vapor of the boiling solvent such as cyclohexanol (158°), p-dichlorobenzene (170°), or dimethyl sulfoxide (183°). During heating, each vessel was withdrawn from the flask periodically and cooled quickly with ice and a salt bath to quench the reaction. The reaction material was diluted with 0.3 ml of deuteriochloroform and then the nmr spectrum of the solution was measured by a Varian A-60 spectrometer (sweep time 500 sec, sweep width 100 cps). The concentration ratios of the isomerized products IIb and IIIb and of Ib were calculated from the proton area of the signal ascribed to the methoxy group of the corresponding compounds. The results obtained were shown in Table IV.

Acknowledgment. We are indebted to Professor R. Hoffmann for his helpful advice. Financial support from Sankyo Co. is also acknowledged.

The Michael Reaction in Nonalkaline Media. V. Effect of Structure on the Rate and Mechanism of Addition of 1,1-Dinitrocarbanions to Methyl Acrylate

Lloyd A. Kaplan* and Hugh B. Pickard

Contribution from the Advanced Chemistry Division,
U. S. Naval Ordnance Laboratory, Silver Spring, Maryland 20910.

Received May 23, 1970

Abstract: The kinetics of the addition of a series of substituted 1,1-dinitromethide ions to methyl acrylate have been studied in 50% dioxane and in water. The requirement for acid catalysis in these Michael additions has been defined as a lowering of the free energy of the transition state for the reversal of the initially formed carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$. This can be accomplished by a substituent R which is able to delocalize negative charge by a resonance interaction. For borderline cases, the rate of protonation of the carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$ may be a deciding factor in effecting a change from an acid catalyzed to an uncatalyzed reaction. A comparison of the specific rate and activation parameters for fluorodinitromethide ion with alkyl, chloro, and hydrogen dinitromethide ions shows that the 2000-fold increase in rate for R = F is due to a 5 kcal mol^{-1} decrease in ΔH^*. This enhanced nucleophilicity is attributed to a destabilization of an sp^2-hybridized carbon by an α-fluorine substituent.

The addition of substituted 1,1-dinitrocarbanions to acrylic systems, in particular methyl acrylate, is well documented in the literature.[1–4] Results of previous kinetic studies of Michael additions to acrylic systems[5–9] suggest the following mechanism for the addition of 1,1-dinitrocarbanions to methyl acrylate. HA is any acid and A$^-$ its conjugate base. When one compares the results obtained in similar buffer solutions with trinitromethane,[5–8] R = NO_2 (p$K \approx 0$[10]), and 1,1-dinitroethane,[9] R = CH_3 (pK = 5.1[10]), a change

$$RC(NO_2)_2^- + CH_2{=}CHCO_2CH_3 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{An^-}{RC(NO_2)_2CH_2{}^-CHCO_2CH_3} \quad (1)$$

$$An^- + HA \underset{k_{A^-}}{\overset{k_{HA}}{\rightleftarrows}} RC(NO_2)_2CH_2CH_2CO_2CH_3 + A^- \quad (2)$$

in the rate-determining step of the reaction is observed. With trinitromethane as the addend, the reaction is subject to general acid catalysis; protonation of the intermediate carbanion An$^-$ is rate determining.[11] However, with 1,1-dinitroethane as the addend,[9] no evidence was found for acid catalysis in phosphate, borate, or carbonate buffers.

To determine if changes in the basicity of the intermediate carbanion An$^-$ caused by varying the substituent R are *solely* responsible for the change in mechanism, we have measured the rates of addition of a

---

(1) H. Shechter and L. Zeldin, *J. Amer. Chem. Soc.*, **73**, 1276 (1951).

(2) L. A. Kaplan, *J. Org. Chem.*, **29**, 2256 (1964).

(3) L. Herzog, K. Klager, and R. D. Geckler, *J. Amer. Chem. Soc.*, 73, 749 (1951).

(4) M. E. Hill, unpublished results from these laboratories.

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

(6) S. S. Novikov, L. A. Nikonova, and V. I. Slovetskii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 395 (1965).

(7) S. S. Novikov, L. A. Nikonova, V. I. Slovetskii, and I. S. Nikonova, *ibid.*, 1066 (1965).

(8) L. A. Kaplan and D. J. Glover, *J. Amer. Chem. Soc.*, **88**, 84 (1966).

(9) S. S. Novikov, L. A. Nikonova, and V. I. Slovetskii, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 1283 (1965).

(10) T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964).

(11) At high acidities, the rate of protonation is increased to the point where the formation of the intermediate carbanion becomes rate determining.[5,8]

series of 1,1-dinitrocarbanions to methyl acrylate in the presence of an acetic acid–acetate buffer system both in 50% dioxane and in water.[12] We have attempted to select the substituent attached to the 1,1-dinitrocarbanion in such a manner as to span a range of σ^* values; *viz.* a range of basicities of the intermediate carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$. Thus, we will compare the rate-determining steps for the addition reaction when $R = NO_2$, $\sigma^*_{C(NO_2)_3} = 4.54$,[13] and $R = CH_3$, $\sigma^*_{CH_3C(NO_2)_2} = 2.76$,[13] as well as other substituents having σ^* values within this range. From a comparison of the activation parameters in 50% dioxane with those in water, a qualitative description of the transition state for this reaction as well as the effect of the substituent R upon the nucleophilicity of the 1,1-dinitrocarbanions will be presented.

Results and Discussion

Kinetic measurements were made under pseudo-first-order conditions in the presence of at least a 100-fold excess of methyl acrylate. With the exception of dinitromethide ion, reaction rates were followed by measuring the change in absorbance at λ_{max} for the 1,1-dinitrocarbanion substrate with time. Pseudo-first-order rate constants were evaluated from plots of log OD *vs.* time, with measurements being made to at least two half-lives. At least one kinetic run for each substrate was allowed to proceed for ten or more half-lives to check for reversibility of the reaction under the conditions used. For all substrates, the OD_∞ value was essentially zero; no evidence for reversibility of the reaction was found. Therefore, reaction 2 is irreversible under the conditions used in this study.

The kinetic runs using dinitromethide ion as the addend required a somewhat different analytical procedure. Since methyl 4,4-dinitrobutyrate ($\lambda_{max}^{pH\ 8}$ 380 nm), the primary product formed in the reaction of dinitromethide ion, λ_{max} (ϵ) 362 nm (20,700), with methyl acrylate has $\epsilon_{362} = 12{,}640$, a plot of log OD_{362} *vs.* time will not yield a straight line. A further complication arises from the fact that methyl 4,4-dinitrobutyrate reacts with methyl acrylate about half as fast as dinitromethide ion under these reaction conditions to yield dimethyl 4,4-dinitroheptanedioate. For dinitromethide ion, the absorbance of the reaction mixture was determined for the same time intervals at 362 and 380 nm and the actual concentration of dinitromethide ion present at various times was calculated from these data. Rate constants were evaluated from plots of log $[HC(NO_2)_2^-]$ *vs.* time.

Besides varying the concentration of methyl acrylate to determine the kinetic order of these additions with respect to methyl acrylate, we also tested each substrate for acid catalysis by varying both the buffer ratio and buffer concentration by a factor of 5–50 for each 1,1-dinitrocarbanion addend used. With the exception of carbomethoxydinitromethide ion in 50% dioxane but not in water and trinitromethide ion in both media,[14] no evidence for acid catalysis was obtained for any of the other 1,1-dinitrocarbanion substrates.

The observation that the addition of carbomethoxydinitromethide ion to methyl acrylate is subject to acid catalysis in 50% dioxane forced us to treat the values of the second-order rate constant k_0, Table I, in a different manner in order to obtain the specific rate of addition, k_1, of carbomethoxydinitromethide ion to methyl acrylate. In an acetic acid–acetate buffer system, we may assume the following mechanism for the overall reaction[8] (eq 3–6).

Table I. Reaction of $^-C(NO_2)_2CO_2CH_3$ with Methyl Acrylate (MeA) and Acetic Acid Buffers in 50% Dioxane[a]

[HOAc]	[OAc⁻]	$10^7[H^+]$[b]	[MeA]	$10^5[S^-]$[c]	10^4k_0, M^{-1} sec⁻¹
		T = 50°			
0.0200	0.100	0.882	0.4530	8.52	1.43
0.100	0.100	4.41	0.4497	7.26	1.57
0.100	0.100	4.41	0.3748	7.26	1.60
0.100	0.0500	8.82	0.4366	8.89	1.68
0.300	0.100	13.2	0.4530	8.52	1.93
0.0600	0.0100	26.4	0.6044	8.89	1.67
0.100	0.0100	44.1	0.6044	8.46	1.72
0.600	0.0300	88.2	0.6549	8.89	2.17
0.600	0.0100	264	0.6044	8.46	2.23
		T = 60°			
0.0200	0.100	0.81	0.4467	7.68	2.57
0.100	0.100	4.06	0.3030	7.62	2.89
0.100	0.100	4.06	0.4545	7.62	2.90
0.0300	0.0100	12.2	0.4467	9.24	2.73
0.300	0.100	12.2	0.4467	7.68	3.43
0.100	0.0100	40.6	0.4467	8.82	3.04
0.300	0.0100	122	0.4467	8.82	3.69

[a] $\mu = 0.1$, sodium perchlorate added when necessary. [b] Calculated from values of K_{HOAc} in 45 w/w% dioxane, $\mu = 0.1$, at these temperatures.[12] [c] $S^- = {}^-C(NO_2)_2CO_2CH_3$.

$$^-C(NO_2)_2CO_2CH_3 + \underset{MeA}{CH_2{=}CHCO_2CH_3} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \underset{An^-}{H_3CO_2CC(NO_2)_2CH_2\bar{C}HCO_2CH_3} \quad (3)$$

$$An^- + H_3O^+ \xrightarrow{k_{H^+}} H_3CO_2CC(NO_2)_2CH_2CH_2CO_2CH_3 + H_2O \quad (4)$$

$$An^- + HOAc \xrightarrow{k_{HOAc}} H_3CO_2CC(NO_2)_2CH_2CH_2CO_2CH_3 + OAc^- \quad (5)$$

$$An^- + H_2O \xrightarrow{k_{H_2O}} H_3CO_2CC(NO_2)_2CH_2CH_2CO_2CH_3 + OH^- \quad (6)$$

Based upon the above equations and the steady-state approximation for the concentration of the intermediate carbanion An^-, the rate of disappearance of carbomethoxydinitromethide ion is given by

$$-\frac{d[^-C(NO_2)_2CO_2CH_3]}{dt} = k_1[^-C(NO_2)_2CO_2CH_3][MeA] \times \frac{\{k_{HOAc}[HOAc] + k_{H^+}[H_3O^+] + k_{H_2O}[H_2O]\}}{k_{-1} + k_{HOAc}[HOAc] + k_{H^+}[H_3O^+] + k_{H_2O}[H_2O]} \quad (7)$$

Equating eq 7 with the experimental rate expression at a given acidity, eq 8, and rearranging terms, the observed

$$-\frac{d[^-C(NO_2)_2CO_2CH_3]}{dt} = k_0[^-C(NO_2)_2CO_2CH_3][MeA] \quad (8)$$

---

(12) For acetic acid in 45% w/w dioxane, $K \approx 5 \times 10^{-7}$ M at 45°; H. S. Harned and G. S. Kazanjian, *J. Amer. Chem. Soc.*, **58**, 1912 (1936).

(13) J. Hine and W. C. Bailey, *J. Org. Chem.*, 26, 2098 (1961).

(14) The addition of trinitromethide ion to methyl acrylate in both 50% dioxane and water has previously been shown to be subject to general acid catalysis.[8]

Table II. Rate Constants and Activation Parameters for the Reaction of $RC(NO_2)_2^-$ with Methyl Acrylate in 50% Dioxane, $\mu = 0.1$

R	10^4k_1, M^{-1} sec^{-1}		ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1}
	30°	50°		
CH_3	17.2 ± 0	67.1 ± 1.7	12.6 ± 0.2	−29.6 ± 0.8
C_2H_5	18.4 ± 0.2	70.7 ± 0.5	12.5 ± 0.1	−29.9 ± 0.3
n-C_4H_9	12.9 ± 0.1	49.5 ± 1.0	12.5 ± 0.2	−30.7 ± 0.7
H	16.0 ± 0.3	60.3 ± 1.2	12.3 ± 0.3	−30.8 ± 0.9
Cl	25.6 ± 0.4	98.5 ± 1.2	12.5 ± 0.2	−29.2 ± 0.6
F	72,400[b]	164,000[b]	7.4 ± 0.3	−30.4 ± 0.9
NO_2[a]	6.39[c]	27.0[c]	13.4[c]	−29.0[c]
CO_2CH_3[a]	0.538[d]	2.41[d]	14.8	−29.3

[a] Acid catalysis observed. [b] Calculated from ΔH^* and ΔS^*; $k_1^{25°} = 5.75 \pm 0.08\ M^{-1}\ sec^{-1}$, $k_1^{35°} = 8.89 \pm 0.04\ M^{-1}\ sec^{-1}$ measured in borax buffers. [c] Calculated from ΔH^* and ΔS^*; data from ref 8. [d] Calculated from ΔH^* and ΔS^*; $10^4k_1^{50°} = 2.41\ M^{-1}\ sec^{-1}$, $10^4k_1^{60°} = 4.97\ M^{-1}\ sec^{-1}$.

Table III. Rate Constants and Activation Parameters for the Reaction of $RC(NO_2)_2^-$ with Methyl Acrylate in Water, $\mu = 0.1$

R	10^4k_1, M^{-1} sec^{-1}		ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1}
	30°	50°		
CH_3	13.5 ± 0.1[a]	65.1[a]	14.4 ± 0.3	−24.2 ± 1.1
C_2H_5	16.1 ± 0.5	75.5 ± 0.6	14.4 ± 0.3	−23.8 ± 1.0
H	19.4 ± 0.1	92.5 ± 1.3	14.6 ± 0.1	−22.9 ± 0.5
Cl	21.4 ± 0.3	100.9 ± 2.3	14.5 ± 0.3	−23.0 ± 0.8
F	49,800 ± 1200	140,000[b]	9.5 ± 0.4	−24.0 ± 1.3
NO_2[e]	6.61[c]	28.2[c]	13.5 ± 0.2	−28.6 ± 0.7
CO_2CH_3	0.628[d]	2.85[d]	14.1 ± 0.4	−31.3 ± 1.2

[a] Data from ref 9; value of $k_1^{50°}$ calculated from ΔH^* and ΔS^*. [b] Calculated from ΔH^* and ΔS^*; $k_1^{15°} = 2.08 \pm 0.05\ M^{-1}\ sec^{-1}$ measured in borax buffers. [c] Calculated from ΔH^* and ΔS^* obtained from data at 20° in 0.4 M hydrochloric acid, $10^4k_1 = 3.17 \pm 0.03\ M^{-1}\ sec^{-1}$, and at 40° in 0.5 M hydrochloric acid, $10^4k_1 = 14.8 \pm 0.3\ M^{-1}\ sec^{-1}$ (ref 6). At these acidities, the secondary reaction yielding methyl 4,4-dinitro-2-hydroxybutyrate makes a negligible contribution to the rate of disappearance of trinitromethide ion (*cf.* ref 8). [d] Calculated from ΔH^* and ΔS^*; $10^4k_1^{40°} = 1.25 \pm 0.02\ M^{-1}\ sec^{-1}$, $10^4k_1^{60°} = 5.20 \pm 0.18\ M^{-1}\ sec^{-1}$. [e] Acid catalysis observed; *cf.* ref 8.

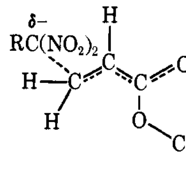
second-order rate constant k_0 has the form

$$k_0 = \frac{k_1[r_1[\mathrm{HOAc}] + [\mathrm{H_3O^+}] + r_2]}{r_3 + r_1[\mathrm{HOAc}] + [\mathrm{H_3O^+}] + r_2} \qquad (9)$$

where $r_1 = k_{HOAc}/k_{H^+}$, $r_2 = k_{H_2O}[H_2O]/k_{H^+}$, and $r_3 = k_{-1}/k_{H^+}$.

Table I gives the values of k_0 obtained for this substrate in various acetic acid–acetate buffers in 50% dioxane. Utilizing a least-squares procedure[15] together with eq 9 and the data in Table I gives values of k_1, r_1, r_2, and r_3 equal to $2.41 \times 10^{-4}\ M^{-1}\ sec^{-1}$, 3.48×10^{-1}, $4.44 \times 10^{-2}\ M$, and $3.17 \times 10^{-2}\ M$ at 50° and $4.97 \times 10^{-4}\ M^{-1}\ sec^{-1}$, 6.10×10^{-1}, $1.67 \times 10^{-1}\ M$, and $1.66 \times 10^{-1}\ M$ at 60°. These values of k_1, r_1, r_2, and r_3 reproduce the observed rate constants k_0 in Table I with an average deviation of 1.9% at 50° and 0.5% at 60°. Dividing the values of r_2 by the concentration of water in 50% dioxane, 28.3 M, gives 1.57×10^{-3} (5.90×10^{-3} at 60°) for the rate constant ratio k_{H_2O}/k_{H^+} at 50°.

Tables II and III summarize the values of the second-order rate constant, k_1, and the activation parameters for the addition of the various 1,1-dinitromethide ion substrates to methyl acrylate in 50% dioxane and in water. Examination of the values of the rate constants in either solvent system shows that with the exception of fluorodinitromethide ion, the specific rate of addition of the remaining dinitromethide ion substrates are accommodated by at most a factor of 50. The rather small spread in the values of k_1, even for substituents such as nitro and carbomethoxy which may delocalize charge by a resonance interaction, suggests that there is little bonding of the dinitromethide ion to methyl acrylate in the transition state for reaction 1 forward. The transition state may be depicted as



in which considerable carbanion character exists on the substituted dinitromethide ion. This makes delocalization of the negative charge by both the α,β-unsaturated system and the dinitromethide ion moieties important contributors to its stabilization.

It is instructive at this point to consider the effect of changing the substituent R upon the magnitude of k_{-1}, the specific rate of reaction 1 reverse. From the principle of microscopic reversibility,[16] the transition state for reaction 1 reverse must be the same as for reaction 1 forward. Substituents which can delocalize negative charge by a resonance interaction will lower the free energy of the transition state. However, such substituents should have a very much smaller effect upon the free energy of the carbanion intermediate $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$, as the dinitromethyl group can only delocalize the negative charge on the α-carbon by an inductive electron withdrawal which is attenuated by an intervening methylene group.[17] Thus, the free energy of the various carbanion intermediates would be about

---

[15] We are indebted to Dr. J. R. Holden of these laboratories for performing this computer operation for us.

[16] J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 73.

[17] This attenuated inductive interaction may possibly make a measurable contribution to the stabilization of the carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$ for those substituents such as nitro and fluoro which have large σ^* values (*cf.* ref 13 and 18).

[18] L. A. Kaplan and H. B. Pickard, *J. Org. Chem.*, **35**, 2044 (1970).

the same and a lowering of the free energy of the transition state results in a lowering of the free energy of activation for the dissociation of the carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$. A corresponding increase in the specific rate, k_{-1}, for reaction 1 reverse would be expected. For reaction 1 forward, substituents which delocalize charge by a resonance interaction will lower the free energy of the ground state more than the transition state. ΔF^* should be larger[19] and the specific rate of addition slower.

In order to apply the aforementioned concepts to the observed mechanism change, uncatalyzed to acid-catalyzed reaction, consider the general expression for the observed second-order rate constant, k_0, at fixed acidity in a general acid catalyzed reaction (eq 10). This is derived from reactions 1 and 2, the steady-state assumption for the concentration of the intermediate carbanion An^- and the assumption that reaction 2 is irreversible. For the limiting condition $k_{-1} \ll \Sigma k_{HA}[HA]$ eq 10 reduces to

$$k_0 = \frac{k_1 \Sigma k_{HA}[HA]}{k_{-1} + \Sigma k_{HA}[HA]} \tag{10}$$

$$k_0 = k_1 \tag{11}$$

and the reaction will not be subject to acid catalysis. However, in the range $k_{-1} \geqq \Sigma k_{HA}[HA]$, either eq 10 or eq 12 obtains and the value of k_0 will increase linearly or

$$k_0 = \frac{k_1 \Sigma k_{HA}[HA]}{k_{-1}} \tag{12}$$

at a decreasing rate as the acidity of the reaction medium increases.

Inspection of the data in Tables II and III shows that the addition of trinitromethide ion to methyl acrylate in both media and the addition of carbomethoxydinitromethide ion in 50% dioxane are subject to general acid catalysis. The addition of the other dinitromethide ion substrates to methyl acrylate is an uncatalyzed reaction. We may consider the reason for this mechanism change in light of the preceding discussion. If 1,1-dinitroethane, uncatalyzed reaction, is chosen as a reference substrate, the limiting condition of eq 11 must apply. On changing R from methyl to nitro or carbomethoxy, the observed change in mechanism must then be due either to a decrease in $\Sigma k_{HA}[HA]$ or an increase in k_{-1} so that the limiting condition $k_{-1} \geqq \Sigma k_{HA} \cdot [HA]$ now applies. A decrease in the specific rate of protonation would be expected if the basicity of the intermediate carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$ decreased markedly whereas a lowering of the free energy of the transition state for reaction 1 would increase k_{-1}.

The increased inductive electron-withdrawing ability of the group $RC(NO_2)_2CH_2-$ as R becomes more electronegative will make the charge on the α carbon of the carbanion $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$ more diffuse. Therefore, the basicities of this series of carbanion intermediates would be expected to vary inversely with the magnitude of σ^* for the group $RC(NO_2)_2CH_2-$. This leads to the ordering $NO_2 < F < Cl < CO_2CH_3 < H \leqq$ alkyl for their relative basicities.[20] As the specific rate of protonation of a homologous series of carbanions should be proportional to their basicities,[21] the partial rate factor $\Sigma k_{HA}[HA]$ for protonation would be expected to increase in the order $NO_2 < F < Cl < CO_2CH_3 < H \leqq$ alkyl. However, in 50% dioxane we observe acid catalysis with trinitromethide and carbomethoxydinitromethide ions as addends, but no catalysis with either fluorodinitromethide or chlorodinitromethide ions. We may conclude at this point that the basicity of the intermediate carbanion is not of prime importance in determining the mechanism of these nucleophilic addition reactions.

The alternative, an increase in the magnitude of k_{-1} for R = NO_2 and CO_2CH_3 relative to the other substituents, would account for the mechanism change observed. Although we cannot obtain values of k_{-1}, and consequently ΔF^*_{-1}, from the kinetic analysis, the values of ΔF^*_1 for R = NO_2 and CO_2CH_3 are 0.6 and 2 kcal mol^{-1} larger than for the remaining substituted dinitromethide ions.[19] As previously stated, a substituent change which produces an increase in ΔF^*_1 will produce a decrease in ΔF^*_{-1} and thereby increase k_{-1}. Though this rationale for the mechanism change holds for R = NO_2 in either solvent system and R = CO_2CH_3 in 50% dioxane, it does not predict the lack of acid catalysis on transferring carbomethoxydinitromethide ion to the aqueous system (see Tables II and III). To account for this change, we have compared the rate constant ratios $k_{H_2O}[H_2O]/k_{-1}$ and k_{HOAc}/k_{-1} for R = NO_2[8] and CO_2CH_3 in 50% dioxane[22] and then transferred them to water to determine how their magnitude changes on going to an aqueous system.

In 50% dioxane, the specific rate ratios for R = CO_2CH_3 are $k_{H_2O}[H_2O]/k_{-1} = 1.2$ and $k_{HOAc}/k_{-1} = 7.5$. The corresponding values for R = NO_2 are 0.15 and 2. For a median [HOAc] = 0.1 *M*, the ratio $\Sigma k_{HA}[HA]/k_{-1}$ is either close to or less than unity for each substrate. Both reactions should be subject to acid catalysis; eq 10 or 12 applies. The change in these specific rate ratios on changing the solvent to water can be estimated from the Brönsted relation, $\log k_{HA} = \alpha \log K_{HA} + \log G$. We have previously defined[8] a modified Brönsted parameter α as the slope of the graph of $\log k_{HA}/k_{H^+}$ *vs.* $\log K_{HA}$ and noted that for trinitromethide ion, this slope, 0.3, is the same for the reaction with methyl acrylate (50% dioxane) or β-nitrostyrene (methanol). A similar treatment of the data for carbomethoxydinitromethide ion gives $\alpha = 0.25$. Assuming $\log G$ to remain essentially constant, then the change in $\log k_{HA}$ is a function of the change in p*K* of the catalyzing acids, water and acetic acid. The ionization constants for these acids increase by 200- and 300-fold, respectively, on going from 50% dioxane to water.[12,23] This corresponds to an increase in the specific rate of protonation of $RC(NO_2)_2CH_2\bar{C}HCO_2CH_3$ by each acid present by about a factor of 4 for R = CO_2CH_3 and a factor 5 for R = NO_2.

---

(19) Excepting fluorine, for those substituents which cannot delocalize charge by a resonance interaction, $\Delta F^*_{303°} = 21.6 \pm 0.1$ kcal mol^{-1} in either solvent system. For nitro and carbomethoxy, $\Delta F^*_{303°}$ is 0.6 and 2 kcal mol^{-1} larger than the average value.

(20) $\sigma^*_{C(NO_2)_3CH_2} = 1.62$,[13] $\sigma^*_{FC(NO_2)_2CH_2} = 1.57$,[18] $\sigma^*_{ClC(NO_2)_2CH_2} = 1.50$,[18] $\sigma^*_{H_3CO_2C(NO_2)_2CH_2} \approx 1.25$ (estimated from $(2\sigma^*_{CH_2NO_2} + \sigma^*_{CH_2CO_2CH_3})/2.8$ or from $(\sigma^*_{CH_3C(NO_2)_2} + \sigma^*_{CH_2CO_2CH_3})/2.8$; ref 13 gives $\sigma^*_{CH_3C(NO_2)_2} = 2.76$) and $\sigma^*_{alkylC(NO_2)_2CH_2} \approx 1.0$.[13]

(21) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1959, p 160 ff.

(22) We have averaged the values of these ratios obtained for each temperature because of uncertainties in the ratios $k_{H_2O}[H_2O]/k_{H^+}$, k_{HOAc}/k_{H^+}, and k_{-1}/k_{H^+} from which they are derived.

(23) H. S. Harned and L. D. Fallon, *J. Amer. Chem. Soc.*, **61**, 2374 (1939).

The effect on the magnitude of the catalytic term $\Sigma k_{HA}[HA]$ on transferring the solvent from 50% dioxane to water would be the following. For R = CO_2CH_3, $k_{H_2O}[H_2O]/k_{-1}$ would increase from 1.2 to about 10.[24] The contribution due to k_{HOAc}, [HOAc] = 0.1 *M*, would increase from 0.75 to 3. Therefore the term $\Sigma k_{HA}[HA]/k_{-1}$ increases from 2 in 50% dioxane to 13 in water.[25] For this substrate, the denominator of eq 10 would change from the limiting condition $k_{-1} \approx \Sigma k_{HA}[HA]$ in 50% dioxane to $k_{-1} \ll \Sigma k_{HA}[HA]$ in water. The reaction would not exhibit acid catalysis as eq 11 would apply.

For R = NO_2, we have calculated that $k_{H_2O}[H_2O]/k_{-1}$ would increase from 0.15 to 1.5 on going from 50% dioxane to water. The term $k_{HOAc}[HOAc]/k_{-1}$ increases from 0.2 to 1.0 at [HOAc] = 0.1 *M*. Therefore, the change in the ratio $\Sigma k_{HA}[HA]/k_{-1}$ is from 0.4 in 50% dioxane, $\Sigma k_{HA}[HA] < k_{-1}$ (eq 12 applies), to 3 in water, $\Sigma k_{HA}[HA] \approx k_{-1}$ (eq 10 applies). Thus, the same solvent change for trinitromethide ion will not change the mechanism from an acid-catalyzed reaction to an uncatalyzed reaction. We conclude that the requirements for acid catalysis in Michael additions are twofold. First the substituents attached to the carbanion addend must be able to delocalize negative charge by a resonance interaction so as to lower the free energy of the transition state for the addition (and reversal) of the carbanion to the α,β-unsaturated system relative to a reference substituent for which the reaction is uncatalyzed. In the absence of sufficient charge delocalization by the substituent, reduced basicity of the intermediate carbanion formed in reaction 1 caused by an inductive electron withdrawal by the substituent can effect a mechanism change.

The data in Tables II and III show that the specific rate of addition, k_1, of carbomethoxydinitromethide ion to methyl acrylate is an order of magnitude less than for trinitromethide ion. The poorer nucleophilicity of carbomethoxydinitromethide ion toward the double bond indicates that the charge on this dinitromethide ion is more delocalized than on trinitromethide ion.[26] Though this conclusion is perhaps surprising, it has been shown that trinitromethide ion is not planar in the crystal.[27] Furthermore, trinitromethane is 2000 times weaker an acid than the vinylog 2-nitrovinyldinitromethane whose conjugate base is planar in solution[28] as well as in the crystal.[29] Therefore, the charge on trinitromethide ion is apparently little delocalized by a resonance interaction with the "nonplanar" nitro group.[27] A rationale for the conclusion that carbomethoxydinitromethide ion is more nearly planar in solution than trinitromethide ion can be made by assuming that there are fewer nonbonded oxygen repulsions in carbomethoxydinitromethide ion than in trinitromethide ion. Replacing a nitro group by a carbomethoxyl group would be expected to reduce these repulsions since the ether oxygen does not bear a formal fractional negative charge as do the nitro oxygen atoms.

It should not be construed that either of these carbanions are planar in solution. By comparison, cyanodinitromethide ion, which is planar in the crystal,[30] does not add to methyl acrylate under these conditions[31] and its conjugate acid has a p*K* = −6.[10] Replacing a nitro group in trinitromethide ion with the linear cyano group significantly reduces oxygen–oxygen repulsions and allows cyanodinitromethide ion to be planar in solution as well as in the crystal.

The presence of an α-fluorine substituent confers enhanced reactivity upon the dinitromethide ion (Tables II and III). The observed 2000-fold increase in the specific rate of addition, k_1, of fluorodinitromethide ion in either solvent is due to a 5 kcal mol^{-1} decrease in ΔH^*. Since ΔS^* for fluorodinitromethide ion is essentially identical with ΔS^* (average) for the other substrates, excepting NO_2 and CO_2CH_3, the observed rate enhancement for fluorodinitromethide ion is not due to differences in the conformation of the ground or transition states for fluorodinitromethide ion relative to the other dinitromethide ion substrates. Large solvation differences between fluorodinitromethide ion and its transition state relative to the other dinitromethide ions may be ruled out as being responsible for the observed rate enhancement, as $\Delta\Delta S^*$ and $\Delta\Delta H^*$ for this substrate are the same as the average values of $\Delta\Delta S^*$ and $\Delta\Delta H^*$.[26] Thus, the 5 kcal mol^{-1} decrease in ΔH^* for fluorodinitromethide ion must be due to destabilization of the ground-state fluorodinitromethide ion. Explanations have been offered for the destabilizing effect of an α-fluorine substituent upon an sp^2-hybridized carbon which involve (a) weakening of the C–F σ bond resulting from the increased electronegativity of an sp^2-hybridized carbon relative to an sp^3-hybridized carbon,[32] and (b) repulsion of the delocalized p electrons in the π system of the carbanion by the p pairs on fluorine.[33] Although no distinction as to which effect is operating to destabilize fluorodinitromethide ion can be made on the basis of the data presented, the magnitude of the α-fluorine effect should be proportional to the degree of planarity of the carbanion. We are cur-

---

(24) Since $[H_2O]$ in water is twice that in 50% dioxane, the term $k_{H_2O}\cdot[H_2O]$ should increase by a factor equal to twice that calculated for the change in pK_{H_2O}.

(25) We have assumed k_{-1} to remain constant on changing the reaction medium. For reaction 1 reverse, charge is more dispersed on the transition state than on the ground-state carbanion $RC(NO_2)_2CH_2\text{-}\bar{C}HCO_2CH_3$. Therefore, transferring the solvent from 50% dioxane to water should decrease k_{-1}; *cf.* J. Hine, "Physical Organic Chemistry," 2nd ed, McGraw-Hill, New York, N. Y., 1962, Section 3.1.f, and references cited therein.

(26) The same conclusion can be reached from a consideration of the activation parameters. For a reaction in which charge concentration occurs on going to the transition state $\Delta\Delta H^*$, $\Delta H^*_{H_2O} - \Delta H^*_{50\%\ \text{dioxane}}$, and $\Delta\Delta S^*$ should be smaller or negative relative to one in which charge is more dispersed in the transition state than in the ground state. For all R's excepting CO_2CH_3 and NO_2, $\Delta\Delta H^* = 2.0 \pm 0.1$ kcal mol^{-1} and $\Delta\Delta S^* = 6.4 \pm 0.6$ cal deg^{-1}. For R = NO_2 and CO_2CH_3, the corresponding values are $\Delta\Delta H^* = 0.1$ and -0.7 kcal mol^{-1} and $\Delta\Delta S^* = 0.4$ and -2.0 cal deg^{-1}. Therefore, there is greater charge concentration on going to the transition state for carbomethoxydinitromethide ion than for trinitromethide ion. Assuming all the transition states to lie at the same position along the reaction coordinate, we conclude that there is greater charge delocalization on carbomethoxydinitromethide ion than on trinitromethide ion.

(27) B. Dickens, *Chem. Commun.*, 246 (1967).

(28) L. A. Kaplan, N. E. Burlinson, W. B. Moniz, and C. Poranski, *ibid.*, 140 (1970).

(29) J. R. Holden and C. Dickinson, *J. Amer. Chem. Soc.*, 90, 1975 (1968).

(30) N. V. Grigor'eva, N. V. Margolis, I. N. Shokhov, I. V. Tselinski, and V. V. Melnikova, *Zh. Strukt. Khim.*, **8**, 175 (1967).

(31) In 50% dioxane with 0.2 *M* methyl acrylate and 0.1 *M* perchloric acid, cyanodinitromethide ion is less than 0.1% reacted in 7 days; *i.e.* $k_1 < 10^{-8}\ M^{-1}\ \text{sec}^{-1}$.

(32) J. Hine, L. G. Mahone, and C. L. Liotta, *J. Amer. Chem. Soc.*, **89**, 5911 (1967).

(33) D. J. Clark, J. N. Murrel, and J. M. Tedder, *J. Chem. Soc.*, 1250 (1963), and W. A. Sheppard, *J. Amer. Chem. Soc.*, **87**, 2410 (1965).

rently exploring the steric perturbation of the α-fluorine effect on carbanion basicity and nucleophilicity.

Experimental Section

Caution! The compounds described in this work are explosives and may detonate on grinding or impact. Appropriate shielding should be used.

Preparation of Reagents. The potassium salts of the dinitromethide ions were prepared by the following procedures: trinitromethide ion,[8] carbomethoxydinitromethide ion,[34] dinitromethide ion from 2,2-dinitro-1,3-propanediol[35] and potassium hydroxide,[36] chlorodinitromethide ion,[10] and alkyl dinitromethide ions from the corresponding 1,1,1-trinitroalkanes by reduction with potassium iodide in methanol.[37] Due to the instability of fluorodinitromethide ion, stock solutions of fluorodinitromethane[38] were used and the pH of the reaction medium adjusted (borax buffers) so that the dinitroalkane was completely dissociated. Control runs, in the absence of methyl acrylate, showed that fluorodinitromethide ion is stable during the time required for the kinetic runs.

Methyl acrylate, dioxane, and other reagents and their stock solutions were prepared as described previously.[8]

Kinetic Procedures.[8] Generally, the appropriate aliquots of buffer components, methyl acrylate, and sodium perchlorate stock solutions were placed in a 100-ml low-actinic volumetric flask and additional solvent was added to a volume of about 90 ml. After thermostating for at least 30 min, a 3–10-ml aliquot of a thermostated dinitromethide ion stock solution was added, the mixture was made up to volume with thermostated solvent and mixed by shaking, and a 1-cm quartz cell was filled with the reaction mixture and placed in the thermostated cell compartment of a Cary Model 14 spectrophotometer. This operation generally took less than 2 min. The optical density of the reaction mixture was continuously monitored with time at λ_{max} for the dinitromethide ion until it had decreased to essentially zero. Pseudo-first- and second-order rate constants were evaluated as described in the Discussion.

For the kinetic runs in water using carbomethoxydinitromethide ion as a substrate, a small correction had to be applied to the pseudo-first-order rate constants due to a slow decomposition reaction at the higher HOAc/OAc$^-$ buffer ratios. For this purpose, an identical control run without methyl acrylate was made for each buffer ratio used in the kinetic study. The pseudo-first-order rate constant for the decomposition reaction was subtracted from the observed pseudo-first-order rate constant for the addition to methyl acrylate. At the lower pH's generated in 50% dioxane, carbomethoxydinitromethide ion was found to be stable throughout the kinetic runs.

Acknowledgment. This work was supported by the Independent Research Fund of the U. S. Naval Ordnance Laboratory, Task IR-44.

---

(34) C. O. Parker, *Tetrahedron*, 17, 109 (1962).

(35) R. B. Kaplan and H. Shechter, *J. Amer. Chem. Soc.*, 83, 3535 (1961).

(36) H. Feuer, G. B. Bachman, and J. P. Kispersky, *ibid.*, 73, 1360 (1951).

(37) D. J. Glover and M. J. Kamlet, *J. Org. Chem.*, 26, 4734 (1961).

(38) M. J. Kamlet and H. G. Adolph, *ibid.*, 33, 3073 (1968).

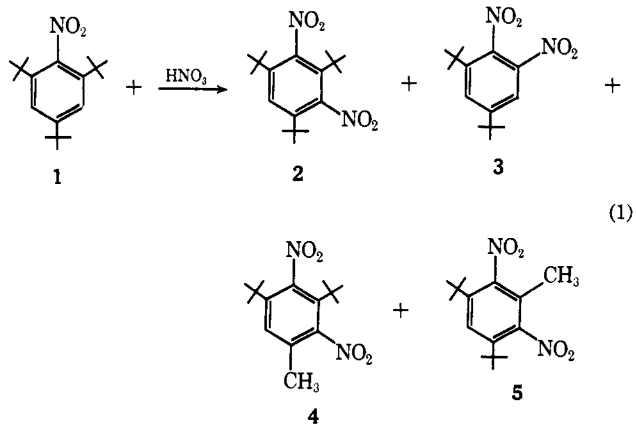
Rearrangement–Fragmentation in Aromatic Nitration

P. C. Myhre,*[1a] M. Beug,[1b] K. S. Brown,[1b] and B. Östman

Contribution from the Department of Chemistry, Harvey Mudd College, Claremont, California 91711, and the Research Institute of National Defense, Dept. 1, Sundbyberg 4, Sweden. *Received October 19, 1970*

Abstract: Two toluene derivatives, 2,4-dinitro-3,5-di-*tert*-butyltoluene (**4**) and 2,6-dinitro-3,5-di-*tert*-butyltoluene (**5**), are formed in 32 and 2% yields, respectively, by nitration of 2,4,6-tri-*tert*-butylnitrobenzene with fuming nitric acid. The paths leading to **4** and **5** are characterized as molecular rearrangements of the intermediate cyclohexadienyl cation **1a** followed by alkyl fragmentation. Deuterium labeling studies establish the intramolecular character of the methyl migration. Nitrogen-15 labeling studies permit identification of the *tert*-butyl group undergoing rearrangement–fragmentation to yield the major fragmentation product, **4**. These data, coupled with kinetic isotope effect data, serve as the basis for discussion of the detailed mechanism of rearrangement–fragmentation.

The nitration of 2,4,6-tri-*tert*-butylnitrobenzene (**1**) yields a diverse set of products, eq 1. The identification of 2,4-dinitro-3,5-di-*tert*-butyltoluene (**4**) and 2,6-dinitro-3,5-di-*tert*-butyltoluene (**5**) among them necessitated a search for a rational mechanistic path.[2] This transformation of a *tert*-butyl group to a methyl group during aromatic nitration seemed most readily explained if one could permit the intermediate cyclohexadienyl cation **1a** to rearomatize to products by two competitive paths, one being molecular rearrangement with fragmentation to yield **4** or **5**, the other being a proton loss to yield 1,3-dinitro-2,4,6-tri-*tert*-butylbenzene (**2**), eq 2.



(1)

Rather special circumstances appear necessary for effective competition of rearrangement–fragmentation with proton loss. Most important of these is a slower than "normal" rate of proton transfer from **1a**. An increase in the barrier to proton transfer could be rea-

---

[1] (a) Address correspondence to this author at Harvey Mudd College; (b) National Science Foundation undergraduate research participants.

(2) At 40°, the observed distribution of products is: **2**, 49%; **3**, 17%; **4**, 32%; and **5**, 2%. More detailed discussion of the distribution data is available in ref 3.

(3) P. C. Myhre, M. Beug, and L. L. James, *J. Amer. Chem. Soc.*, 90, 2105 (1968).