where pyridinium nitrate did not precipitate, the solvent was reduced to one-half its original size and four times that volume of ether was added. This solution was extracted three times with equal volumes of water and the ethereal layer was then separated and dried over sodium sulfate. The crude residue left after the ether was removed was chromatographed on silica gel using hexane as an eluent.

Inspection of all the crude reaction products was done by infrared and nuclear magnetic resonance spectra. The amount of deuterium incorporated was determined from nuclear magnetic resonance spectra or from mass spectra. 1-Nitro-2-methyl-2-pentyl nitrate, 1-nitro-2,4,4-trimethyl-2-pentyl nitrate,[12] and 1-nitro-2-methyl-2-propyl nitrate[13] have been described previ-

(12) J. M. Larkin and K. L. Kreuz, *J. Org. Chem.*, **37**, 3079 (1972).

(13) N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, 52 (1948).

ously, as has 1-nitro-2-methyl-1-propene.[14] The elemental analysis for 1-nitro-1-decene and 1-nitro-2-methyl-1-pentene are given below.

		C	H	N
$C_{10}H_{19}NO_2$	Calcd	64.9	10.4	7.57
	Obsd	64.5	10.5	7.30
$C_6H_{11}NO_2$	Calcd	55.8	8.60	10.9
	Obsd	55.4	9.00	10.9

Registry No.—1, 36601-57-7; 2, 35223-51-9; 3, 14202-69-8; 5, 36601-60-2; 9, 36601-61-3; 10, 36601-62-4; 11, 1606-30-0.

(14) A. Lambert and A. Lowe, *ibid.*, 1517 (1947).

The Use of an α-Fluorine Substituent as a Transition State Probe in Base-Catalyzed Nitrous Acid Eliminations

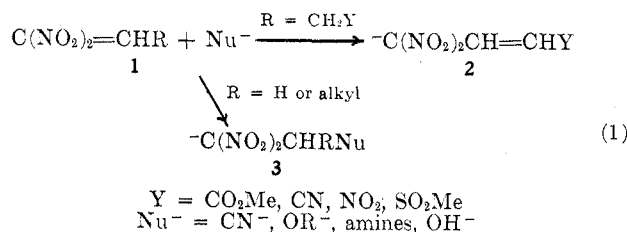LLOYD A. KAPLAN* AND NICHOLAS E. BURLINSON

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The results of a study of the kinetics and mechanism of the reaction of 4,4,4-trinitrobutyronitrile and 4,4-dinitro-4-halobutyronitriles with base have shown that the isolated products are derived from an extremely reactive 1,1-dinitro- or 1-halo-1-nitroethylene intermediate. The α-fluorine effect has been utilized as a transition state probe to show that the mechanism by which the olefin intermediate forms is a nonreversible, second-order carbanion β elimination of the elements of nitrous acid.

The reaction of 1,1,1-trinitroethyl compounds with bases[1-6] has been viewed as yielding a 1,1-dinitroethylene intermediate 1.[1] The fate of this reactive intermediate depends upon the nature of the substituent attached to the carbon α to the dinitromethyl group (eq 1). When R = CH₂Y, where Y is a con-

$$C(NO_2)_2{=}CHR + Nu^- \xrightarrow{\quad R\ =\ CH_2Y \quad} {^-C(NO_2)_2CH{=}CHY}$$
$$\mathbf{1} \qquad\qquad\qquad\qquad\qquad \mathbf{2}$$
$$\searrow R\ =\ H\ \text{or alkyl}$$
$$^-C(NO_2)_2CHRNu \qquad (1)$$
$$\mathbf{3}$$
$$Y = CO_2Me,\ CN,\ NO_2,\ SO_2Me$$
$$Nu^- = CN^-,\ OR^-,\ \text{amines},\ OH^-$$

jugatively electron-withdrawing substituent, the olefin 1 loses an α-methylene proton to form the planar[7] carbanion 2. When this path is not available, nucleophilic addition to the double bond occurs to form the adduct 3. Though the olefin 1 has never been isolated from these base-catalyzed eliminations, its rate of formation might be expected to be slow relative to subsequent reactions. Thus, a combination of kinetic and trapping experiments should enable us to determine if 1 is the precursor of 2 and 3.

We also planned to utilize the α-fluorine effect[8,9]

(1) L. Zeldin and H. Shechter, *J. Amer. Chem. Soc.*, **79**, 4708 (1957).

(2) J. Meisenheimer and M. Schwarz, *Chem. Ber.*, **39**, 2546 (1906).

(3) J. Meisenheimer, *ibid.*, **36**, 434 (1903).

(4) M. J. Kamlet and J. C. Dacons, *J. Org. Chem.*, **26**, 3005 (1961).

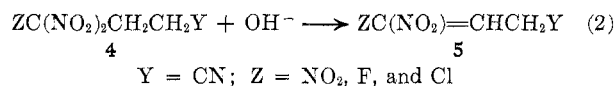(5) L. A. Kaplan, *ibid.*, **29**, 2256 (1964).

(6) M. J. Kamlet, J. C. Dacons, and J. C. Hoffsommer, *ibid.*, **26**, 4881 (1961).

(7) L. A. Kaplan, N. E. Burlinson, W. B. Moniz, and C. Poranski, *Chem. Commun.*, 140 (1970).

(8) L. A. Kaplan and H. B. Pickard, *ibid.*, 1500 (1969); L. A. Kaplan and H. B. Pickard, *J. Amer. Chem. Soc.*, **93**, 3447 (1971).

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

as a probe to determine the structure of the transition state for this nitrous acid elimination reaction (eq 2).

$$ZC(NO_2)_2CH_2CH_2Y + OH^- \longrightarrow ZC(NO_2){=}CHCH_2Y \quad (2)$$
$$\mathbf{4} \qquad\qquad\qquad\qquad\qquad\qquad \mathbf{5}$$
$$Y = CN;\ Z = NO_2,\ F,\ \text{and Cl}$$

If the formation of 5 requires concerted C–H and C–NO₂ bond breaking in the transition state, then the γ carbon atom, ZC(NO₂)₂⁻, has more s character in the transition state than in the ground state and ΔH^*, but not necessarily ΔF^*,[8] for Z = F should be larger than for Z = NO₂ or Cl.[8,9] Alternatively, if only carbanion formation occurs in the rate-determining step,[10] then the hybridization of the γ carbon atom will be the same in the ground and transition states and ΔH^*[8] for Z = F and NO₂ should be essentially the same.[11] The twofold effect of the enhanced acidity of the β hydrogen atoms due to the strongly electron-withdrawing ZC(NO₂)₂ function and the presence of a good leaving group, nitro departing as resonance-stabilized nitrite ion, might be expected to make the elimination of nitrous acid from the substrates 4 proceed by a nonreversible carbanion mechanism rather than an E2 or a reversible E1cB mechanism.

Results and Discussion

The Overall Reaction.—Prior to making kinetic measurements, we carefully investigated the reaction of the substrates 4 with hydroxide. Since they have
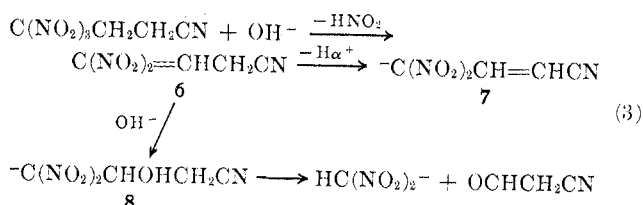
(10) For a description of the various mechanisms for base-catalyzed β eliminations, see F. G. Bordwell, M. M. Vestling, and K. C. Yee, *J. Amer. Chem. Soc.*, **92**, 5950 (1970), and references cited therein.

(11) Since the σ* values for FC(NO₂)₂ and C(NO₂)₃, 4.4[12] and 4.5,[13] are about equal, large differences in ΔH^* cannot be attributed to differences in Cβ–H bond strengths.

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

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

two sites, C_β H_2 and C_α H_2, bearing acidic protons, the possibility existed that the desired reaction would be complicated by a retrograde Michael reaction yielding the Z-substituted dinitromethide ion and acrylonitrile.[14] When 4, Z = NO_2, was allowed to react with hydroxide at spectrophotometric concentrations, a comparison of the spectrum of the reaction mixture with that of authentic 7 indicated the presence of a second species absorbing between 350 and 380 nm. After subtraction of the absorbance contribution of 7 from the spectrum of the reaction mixture, the residual absorbance peaked at 362 nm. The position of this maximum is coincident with that of dinitromethide ion.[15] The formation of dinitromethide ion together with 7 can be rationalized by the following sequence in which the

$$C(NO_2)_3CH_2CH_2CN + OH^- \xrightarrow{-HNO_2}$$
$$C(NO_2)_2{=}CHCH_2CN \xrightarrow{-Ha^+} {}^-C(NO_2)_2CH{=}CHCN$$
$$\underset{6}{} \qquad\qquad\qquad \underset{7}{}$$
$$OH^- \Big/ \tag{3}$$
$$\Big\downarrow$$
$${}^-C(NO_2)_2CHOHCH_2CN \longrightarrow HC(NO_2)_2{}^- + OCHCH_2CN$$
$$\underset{8}{}$$

addition product 8 dissociates to form dinitromethide ion.[16]

From the stoichiometry of the reaction (eq 3), there should be a 1:1 correspondence between the concentrations of 7 plus dinitromethide ion and nitrite ion. Several reaction mixtures were assayed for nitrite ion as well as the dinitrocarbanion species formed. The data are presented in Table I.

TABLE I

REACTION OF 4.98×10^{-5} M $C(NO_2)_3CH_2CH_2CN$ WITH OH^- IN WATER AT $25°$

Buffer[a]	pH	$10^5[7]$[b]	$10^5[HC(NO_2)_2{}^-]$[b]	$10^5[NO_2{}^-]$[c]
B, 0.01/0.04	9.66	4.14	0.52	5.40
B, 0.015/0.035	9.46	4.12	0.58	5.36
B, 0.005/0.045	9.79	4.12	0.58	5.36
C, 0.007/0.018	9.54	3.91	0.74	5.30

[a] B = Borax–hydroxide, C = bicarbonate–hydroxide, [HA]/[A$^-$] in M. [b] Calculated from absorbance measurements at 320 nm λ_{max} 7, and 362, λ_{max} $HC(NO_2)_2{}^-$. Average $[7 + HC(NO_2)_2{}^-] = 4.68 \pm 0.02 \times 10^{-5}$ M. [c] Average $[NO_2{}^-] = 5.36 \pm 0.03 \times 10^{-5}$ M.

Inspection of the data shows both the concentrations of nitrite and 7 plus $HC(NO_2)_2{}^-$ to be remarkably constant. However, the average value of the sum of the carbanion concentrations is 6% less than theoretical, 4.98×10^{-5} M, and the average value of the nitrite concentration is about 8% greater. As both 7 and dinitromethide ion are stable in the reaction medium, either 4,4,4-trinitrobutyronitrile or the intermediates 6 or 8 denitrosate under these conditions. Nucleophilic attack on the trinitromethyl group of the substrate molecule by hydroxide ion can be ruled out, as this would produce nitrate rather than nitrite together

(14) The reaction of 4, Y = CO$_2$Me and Z = NO$_2$, with bases produced trinitromethide ion and the carbanion $^-$C(NO$_2$)$_2$CH$_2$CHOHCO$_2$Me together with 2, Y = CO$_2$Me. See L. A. Kaplan and D. J. Glover, *J. Amer. Chem. Soc.*, **88**, 84 (1966).

(15) M. J. Kamlet and D. J. Glover, *J. Org. Chem.*, **27**, 537 (1962).

(16) P. Duden and G. Ponndorf, *Chem. Ber.*, **38**, 203 (1905); L. Herzog, M. H. Gold, and R. D. Geckler, *J. Amer. Chem. Soc.*, **73**, 749 (1951); H. Feuer, G. B. Bachmann, and W. May, *ibid.*, **76**, 5129 (1954); T. N. Hall, *J. Org. Chem.*, **29**, 3587 (1964).

with 4,4-dinitrobutyronitrile.[1,17] Since the formation of 6 will be shown to be rate determining, partitioning it among several side reactions will not affect the measurement of its specific rate of formation.

In a similar fashion, 4, Z = F or Cl, reacted with hydroxide ion to form the 4-fluoro-4-nitro and 4-chloro-4-nitro analogs of 7. On a synthetic scale, it was not possible to isolate the potassium salts of these carbanions, as they were not stable. However, they were formed quantitatively at spectrophotometric concentrations, since a mole for mole correspondence between nitrite ion formed in the reaction and the initial concentration of halodinitrobutyronitrile was obtained. The absorptions of these carbanions in the ultraviolet were consistent with structures analogous to 7 (Table II).

TABLE II

ULTRAVIOLET ABSORPTION MAXIMA FOR $^-ZC(NO_2)CH{=}CHY$[a]

Z	Y = CN	Registry no.	Y = CO$_2{}^-$	Registry no.
Cl	342 (13,800)[b]	36529-35-8	322 (16,400)[c]	36488-77-4
F	335 (23,000)[b]	36529-36-9	317 (19,500)[c]	36488-78-5
NO$_2$	320 (19,300)[c,d]	26881-30-1	313 (16,000)[c,e]	36529-38-1

[a] ϵ values in parentheses. [b] In 0.2 M sodium hydroxide, ϵ values based on the concentration of halodinitrobutyronitrile. [c] In 0.01 M sodium hydroxide. [d] Long wavelength maximum at 395 nm (ϵ 9800). [e] Long wavelength maximum at 410 nm (ϵ 8300).

Corroboration of these structural assignments was obtained from the reaction products of the corresponding acids 4, Y = CO$_2$H, with hydroxide ion. Isolable dipotassium salts of 4-fluoro-4-nitro- and 4-chloro-4-nitro-2-butenoic acids were obtained. The nmr spectra of these salts (Table III) are of the AB or the ABX,

TABLE III

100-MHz NMR SPECTRA OF $^-ZC(NO_2)CH_B{=}CH_ACO_2{}^-$ IN D_2O[a]

Z	δ_{HA}	δ_{HB}
F	6.362 6.380, 6.517, 6.532	7.497, 7.650, 7.730, 7.886
Cl	6.464, 6.615	8.060, 8.213
NO$_2$	6.884 7.040	8.106 8.263

[a] External TMS reference in capillary insert, 30°.

X = F, type with $J_{AB} = 15$–16 Hz. The magnitude of J_{AB} is consistent with a trans configuration of the substituents attached to the double bond. The assignments of the lines in Table III for Z = Cl and NO$_2$ were made by comparison with the positions of the lines in the spectrum of Z = F. For this carbanion, the upfield multiplet had $J = 1.5$ Hz. The smaller J_{HF} value would be expected for the longer range J_{H_AF} coupling.

Kinetics of the Reaction.—Reaction rates for the three nitrile substrates 4 were measured under pseudo-first-order conditions either in excess sodium hydroxide or in buffer solutions of an appropriate pH. The rate of appearance of the 4-Z-4-nitro-2-butenenitrile elimination product was followed in the ultraviolet (Table II). Pseudo-first-order rate constants were evaluated from the slopes of plots of log $(OD_\infty - OD_t)$ vs. time. These plots were found to be linear for at least 3 half-

(17) D. J. Glover, *J. Phys. Chem.*, **74**, 21 (1970).

TABLE IV

REACTION OF $ZC(NO_2)_2CH_2CH_2CN$ WITH HYDROXIDE ION, $\mu = 0.1$

[HA]^a	[A$^-$]	pH	10^5[OH$^-$]^b	k_2, M^{-1} sec^{-1}		[HA]^a	[A$^-$]	pH	10^5[OH$^-$]^b	k_2, M^{-1} sec^{-1}
			Z = NO$_2$, T = 25°					11.706^d	834	0.193
C, 0.010	0.015	10.13	22.1	24.0				11.716	853	0.189
C, 0.015	0.010	9.79	10.1	23.7				11.716^e	853	0.191
C, 0.020	0.005	9.37	3.85	23.3				11.726	873	0.190
C, 0.034	0.016	9.67	7.67	24.6				11.798	1030	0.190
B, 0.020	0.080	9.70	8.22	23.1				11.807	1050	0.189
B, 0.015	0.035	9.44	4.52	23.3				11.826	1100	0.181
B, 0.010	0.040	9.66	7.50	23.6					Average	0.190 ± 0.004
B, 0.005	0.045	9.79	10.1	24.0						
B, 0.0025	0.0225	9.84	11.4	24.3				Z = F, T = 40°		
				Average 23.8 ± 0.4^f		P, 0.020	0.005	10.665	214	0.813
						P, 0.020	0.005	10.657	210	0.818
			Z = NO$_2$, T = 40°			P, 0.015	0.010	11.022	486	0.793
C, 0.020	0.005	9.250	8.22	95.8		P, 0.015	0.010	11.028	493	0.780
C, 0.020	0.005	9.278	8.77	95.5		P, 0.015	0.010	11.026	491	0.783
C, 0.020	0.005	9.301	9.25	91.0		C, 0.010	0.015	10.129	62.2	0.791
C, 0.015	0.010	9.667	21.5	91.4					Average	0.796 ± 0.013
C, 0.015	0.010	9.690	22.7	90.1						
C, 0.010	0.015	9.944	40.6	96.6				Z = Cl, T = 25°		
C, 0.010	0.015	9.986	44.8	93.6		P, 0.0005	0.0102	11.685	794	0.111
B, 0.045	0.005	8.178	0.697	100		P, 0.0023	0.0102	11.420	432	0.114
B, 0.040	0.015	8.622	1.94	98.7				11.838	1130	0.113
B, 0.040	0.010	8.410	1.19	99.4				12.019	1710	0.118
B, 0.030	0.020	8.800	2.92	96.7				12.019^c	1710	0.114
B, 0.030	0.020	8.795	2.88	98.9					Average	0.114 ± 0.002
				Average 95.6 ± 2.8^f						
								Z = Cl, T = 40°		
			Z = F, T = 25°			P, 0.020	0.005	10.652	208	0.615
		11.496	514	0.198		P, 0.015	0.010	11.011	474	0.620
		11.505	525	0.183		P, 0.010	0.015	11.208	746	0.621
P, 0.0022	0.0103	11.585	631	0.187		P, 0.010	0.015	11.243	809	0.620
		11.657	745	0.200		C, 0.003	0.022	10.425	123	0.631
		11.706^c	834	0.191					Average	0.616 ± 0.004

^{a} C = HCO_3^-/CO_3^{2-}, B = $H_3BO_3/H_2BO_3^-$, P = HPO_4^{2-}/PO_4^{3-}. No entry indicates that an appropriate aliquot of 0.10 M sodium hydroxide was used in place of the buffer. Substrate concentrations are 10^{-4} to 5×10^{-5} M. ^{b} pK water at ionic strength = 0.1; 13.785 (25°) and 13.335 (40°). H. S. Harned and W. J. Hamer, *J. Amer. Chem. Soc.*, 55, 2194 (1933). ^{c} NaBr used instead of NaClO$_4$ to adjust ionic strength to 0.1. ^{d} As in c but NaCl used. ^{e} As in c but Na$_2$S$_2$O$_3$ used. ^{f} Statistically corrected for three nitro groups; $k_2^{25°} = 15.9 \pm 0.3$ M^{-1} sec^{-1} and $k_2^{40°} = 63.7 \pm 1.9$ M^{-1} sec^{-1}.
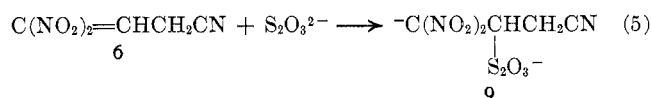
lives and were generally good quality straight-line plots for 5 half-lives. For some of the kinetic runs using 4,4,4-trinitrobutyronitrile as the substrate, the actual concentrations of the carbanion 7 and dinitromethide ion were calculated from the change in absorbance at 320 and 362 nm with time. Rate constants evaluated from either product species and the initial concentration of 4,4,4-trinitrobutyronitrile were found to be identical with those obtained by graphing log (OD$_\infty$ − OD$_t$) vs. time. Although the values of the first-order constants varied with the hydroxide concentration, dividing them by the hydroxide concentration gave k_2 (Table IV), which is constant over the range of hydroxide concentrations studied. These observations are described by the rate expression eq 4.

$$-d[4]/dt = k_2[4][OH^-] \qquad (4)$$

The first-order dependency of the rate on the hydroxide concentration indicated that k_2 described the specific rate of nitrous acid elimination from the substrates 4. Additional evidence for this conclusion came from the results of trapping experiments. From the data in Table I, about 10% of the product formation occurs by nucleophilic addition to the double bond of 6 (eq 3). If hydroxide is acting as a nucleophile to form 8 and a base to form 7, then generating the olefin 6 in the presence of thiosulfate ion at a concentration

equal to or greater than the hydroxide concentration should divert all of 6 to the addition path, as thiosulfate ion is about 150 times more reactive as a nucleophile[18] and about 10^{12} times weaker a base than hydroxide.[19]

When 4,4,4-trinitrobutyronitrile was treated with hydroxide (HCO$_3^-$/CO$_3^{2-}$) in the presence of excess thiosulfate ion, the ultraviolet spectrum of the reaction mixture exhibited an absorption maximum at 368 nm that increased with time.[20] The position of this maximum is consistent with 9,[21] the product ex-

$$C(NO_2)_2{=}CHCH_2CN + S_2O_3^{2-} \longrightarrow {}^-C(NO_2)_2CHCH_2CN \qquad (5)$$
$$\underset{6}{} \qquad \qquad \underset{\overset{|}{S_2O_3^-}}{\underset{9}{}}$$

(18) Using methyl bromide as the reference substrate: C. G. Swain and C. B. Scott, *J. Amer. Chem. Soc.*, 75, 141 (1953).

(19) If one compares the pK of HS$_2$O$_3^-$, ~2 [F. M. Page, *J. Chem. Soc.*, 1719 (1953)], and water.

(20) Neither 4,4-dinitro-4-fluoro- nor 4,4,4-trinitrobutyronitrile reacted with 1 M thiosulfate ion at pH's less than 7. Even in nonalkaline media, the 4-chloro derivative was reduced to 4,4-dinitrobutyrontrile. Similar changes in the site of attack of nucleohiles have been observed previously: L. A. Kaplan in "The Chemistry of the Nitro and Nitroso Groups," Vol. II, H. Feuer, Ed., Wiley, New York, N. Y., 1970, p 321; cf. ref 1. With thiosulfate ion at pH ~12, 4, Z = F, yielded only the 4-fluoro-4-nitro analog of 7. The inability of the fluoro derivative to form an addition product of the type 9 can be attributed to the reduced susceptibility of the double bond in 5, Z = F, to nucleophilic attack on replacing the conjugatively electron-withdrawing nitro group by fluorine.

(21) Carbanions of the general structure $^-$C(NO$_2$)$_2$CHZCH$_2$Y, Y = CN, SO$_2$Me, CO$_2$Me, etc., and Z = substituent with unshared p pairs as OMe, have absorption maxima between 360 and 370 nm.[15]

pected from the addition of thiosulfate ion to the olefin 6. The absorbance at 368 nm went through a maximum, and concurrent with the decrease in absorption at 368 nm, new absorption maxima began to develop at ~325 and ~400 nm. On prolonged standing, the spectrum of the reaction mixture became identical with that of the dinitro carbanion 7. The overall reaction appeared to involve a rapid conversion of 4,4,4-trinitrobutyronitrile to 9 followed by a slow transformation of 9 to 7.

It was not possible to obtain good quality pseudo-first-order plots for the rate of formation of 9 by graphing log ($[9]_\infty - [9]_t$) vs. time, as the infinity value was not constant owing to the simultaneous conversion of 9 to 7. However, if the specific rate of conversion of 9 to 7, k_N (Table V), is at least tenfold slower than its

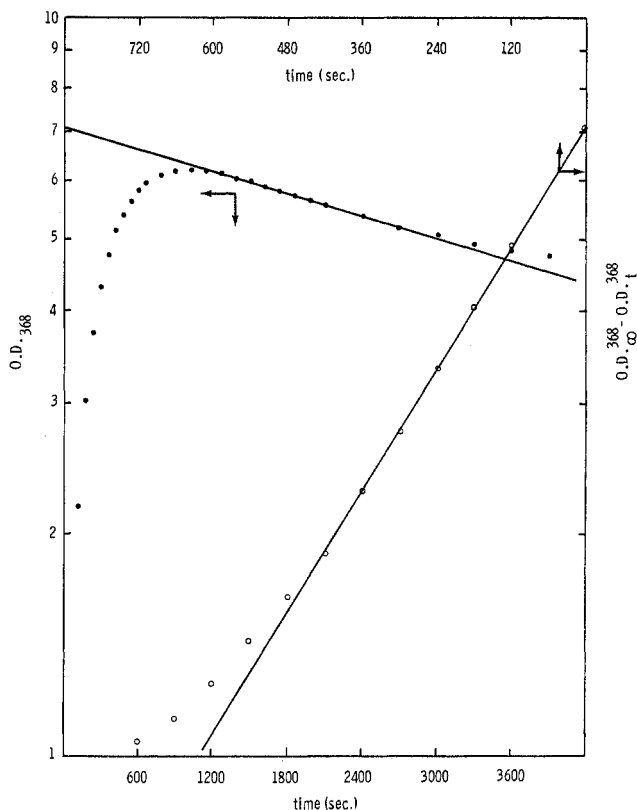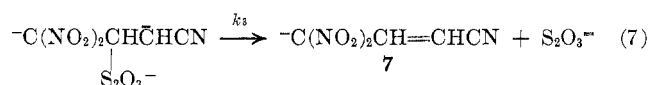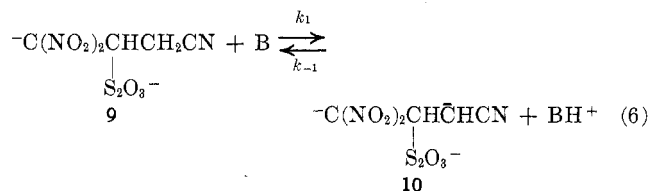Figure 1.—Log OD_{368} vs. time for the formation and disappearance of 9 (●); log $[(OD_{368})_\infty - (OD_{368})_t]$ vs. time for the formation of 9 (○). See run 9 in Table V for reagent concentrations.

Table V

Reaction of $C(NO_2)_3CH_2CH_2CN$ with OH^- in the Presence of $S_2O_3{}^{2-}$, 25°, $\mu = 0.1$

Run	$[HA]^a$	$[A^-]$	$[S_2O_3{}^{2-}]$	pH	$10^5[OH^-]$	k_2, M^{-1} sec^{-1}	$10^4 k_N$, sec^{-1}
1	0.020	0.005	0.012	9.40	4.12	22.4	0.402
2	0.020	0.005	0.023	9.42	4.32	24.8	0.452
3	0.016	0.009	0.022	9.70	8.22	25.1	0.788
4	0.016	0.009	0.022	9.70	8.22	25.5	0.795
5	0.020	0.020	0.014	9.97	15.3	23.1	1.79
6	0.020	0.020	0.007	9.98	15.7	25.7	1.81
7	0.010	0.015	0.013	10.10	20.7	23.7	2.03
8	0.006	0.006	0.025	9.95	14.6	23.6	0.787
9	0.013	0.012	0.021	9.94	14.3	22.0	1.13
10	0.021	0.019	0.014	9.95	14.6	24.3	1.72
11	0.026	0.024	0.009	9.92	13.7	24.7	1.90

^{a} $HCO_3^-/CO_3{}^{2-}$ buffers.

formation, $k_2[OH^-]$ (Table V), then a good approximation of $[9]_\infty$ can be had by extrapolating the slope of the graph of log [9] vs. time for the conversion of 9 to 7 to zero time. In excess buffer, this reaction was found to be pseudo-first-order. A further complication arose from the fact that the product 7 has a molar extinction of 6400 at 368 nm, λ_{max} for 9.[22] Therefore, plots of log OD_{368} vs. time will tend to develop upward curvature as the conversion of 9 to 7 progresses. Since it was not possible to isolate 9 so as to obtain an accurate value of its molar extinction for use in calculating the actual concentration of 9 in the 9 and 7 mixture, the initial slope of the log OD_{368} vs. time plots was used for this extrapolation. Figure 1 presents the log OD_{368} profile vs. time for a typical kinetic run together with the zero time extrapolation.

Using the extrapolated zero time value as $(OD_{368})_\infty$, k_ψ, the pseudo-first-order constant for the formation of 9, was evaluated from the slope of the graph of log $[(OD_{368})_\infty - (OD_{368})_t]$ vs. time. These plots usually exhibited upward curvature about the beginning of the third half-life (Figure 1). This was expected, since the rate of conversion of 9 to 7 late in the reaction becomes appreciable and makes the observed $(OD_{368})_t$ less and hence $(OD_{368})_\infty - (OD_{368})_t$ greater than that calculated for a simple first-order rate of formation.

Table V summarizes the values of k_2, $k_\psi/[OH^-]$, for the conversion of 4,4,4-trinitrobutyronitrile to 9. The average value of k_2, 24.1 ± 1.0 M^{-1} sec^{-1}, agrees exceptionally well with the value obtained in the absence of thiosulfate ion (Table IV). Therefore, in spite of the difference in the products formed in the presence and absence of thiosulfate ion, the formation of the olefin 6 is rate determining for both reactions.

The conversion of 9 to 7 is a rather interesting transformation. Over the pH range studied, 9 should be present as the dianion.[23] Inspection of the values of the pseudo-first-order constant k_N in Table V shows a dependency of the specific rate on both the hydroxide, runs 1, 2, and 8, and buffer base, runs 8–11, concentrations but not on the thiosulfate concentration, runs 1, 2, 5, and 6. A mechanism in which proton abstraction from 9 is rate determining is consistent with these observations (eq 6 and 7). The conversion of the tri-
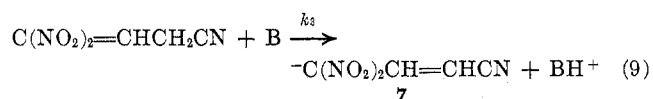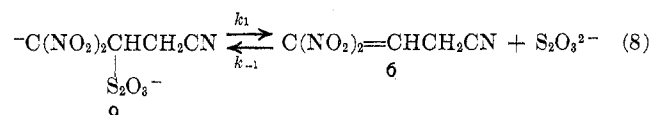
$$\begin{array}{c}{}^-C(NO_2)_2CHCH_2CN + B \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \\ \underset{\substack{|\\ S_2O_3^-\\ \mathbf{9}}}{} \end{array}$$

$$\begin{array}{c}{}^-C(NO_2)_2CH\bar{C}HCN + BH^+ \quad (6)\\ \underset{\substack{|\\ S_2O_3^-\\ \mathbf{10}}}{}\end{array}$$

$$\begin{array}{c}{}^-C(NO_2)_2CH\bar{C}HCN \overset{k_3}{\longrightarrow} {}^-C(NO_2)_2CH{=}CHCN + S_2O_3^- \quad (7)\\ \underset{\substack{|\\ S_2O_3^-}}{} \qquad\qquad \mathbf{7}\end{array}$$

anion 10 to 7 occurs rapidly, as thiosulfate ion is a good leaving group. The question of the magnitude of k_{-1}

(22) For 9, we estimate ϵ_{368} ~ 14,000. This is based on the extrapolated value of $(O.D._{368})_\infty$ for the formation of 9 and the initial concentration of 4,4,4-trinitrobutyronitrile. Carbanions of the type $^-C(NO_2)_2CHOMe$-CH_2Y, $Y = CO_2Me$, CN, and SO_2Me, have ϵ 14–16,000; unpublished results.

(23) The pK's of 1,1-dinitroalkanes are less than 6 [M. E. Sitzman, H. G. Adolph, and M. J. Kamlet, *J. Amer. Chem. Soc.*, 90, 2815 (1968)] and the pK of $HS_2O_3^-$ is ~2.[19]

[BH$^+$] relative to k_3 was answered by generating **9** in a buffered deuterium oxide–dioxane solvent system and allowing it to convert to **7** under these conditions. Since no deuterium uptake was observed at the α carbon atom of **7**, $k_3 \gg k_{-1}$[BH$^+$] and the conversion of **9** to **7** occurs by a nonreversible carbanion mechanism.

Mechanisms involving a unimolecular displacement of thiosulfate ion from **9** (eq 8 and 9) can be ruled out

$$^-C(NO_2)_2CHCH_2CN \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} C(NO_2)_2{=}CHCH_2CN + S_2O_3{}^{2-} \quad (8)$$
$$\underset{\underset{\mathbf{9}}{S_2O_3{}^-}}{|} \qquad\qquad\qquad \mathbf{6}$$

$$C(NO_2)_2{=}CHCH_2CN + B \overset{k_3}{\longrightarrow}$$
$$^-C(NO_2)_2CH{=}CHCN + BH^+ \quad (9)$$
$$\mathbf{7}$$

on the following grounds. If k_{-1}[S$_2$O$_3{}^{2-}$] $\gg k_3$[B], then k_N should decrease on increasing the thiosulfate ion concentration at constant pH and buffer base concentration. For the inverse, k_{-1}[S$_2$O$_3{}^{2-}$] $\ll k_3$[B], **9** would not initially form from **6** and thiosulfate ion.

Mechanisms for the formation of the olefins **5** that are kinetically second order can be divided into two categories:[10] those requiring some degree of C–NO$_2$ bond breaking and double bond formation in the transition state (concerted E2) and those in which carbanion formation is rate determining. To distinguish between the two categories, we have applied the α-fluorine effect[8,9] as a transition-state probe. As previously stated,[8,9] a process in which a ground-state carbon atom bearing a fluorine substituent gains s character on going to the transition state should be energetically disfavored relative to the nonfluorine-substituted carbon atom. Thus, for the substrates **4**, the ordering of ΔH^* values should be NO$_2$ < Cl < F for a concerted process in which both C–NO$_2$ bond breaking and double bond formation make a contribution to the transition state.[24] The data in Table VI do not give rise to such an order-

TABLE VI
ACTIVATION PARAMETERS FOR THE REACTION
ZC(NO$_2$)$_2$CH$_2$CH$_2$CN + OH$^-$

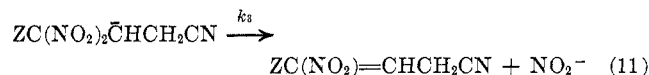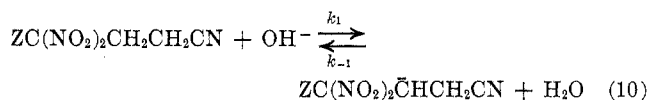| Z	k_2, M^{-1} sec^{-1} (25°)	ΔH^*, kcal mol^{-1}	ΔS^*, cal deg^{-1}
NO$_2$	15.9 ± 0.3^a	16.6 ± 0.4^a	2.5 ± 1.4^a
F	0.190 ± 0.004	17.1 ± 0.3	−4.4 ± 1.1
Cl	0.114 ± 0.002	20.3 ± 0.2	5.1 ± 0.7

^{a} Calculated from the statistically corrected values of k_2; Table IV, ref f.

ing. From this we conclude that neither C–NO$_2$ bond breaking nor double-bond formation has occurred to a significant extent in the transition state for the formation of **5**.

Mechanisms of the second category are those in which carbanion formation precedes C–NO$_2$ bond breaking

(24) An estimate of the magnitude of the effect of an α-fluorine substituent on ΔH^* is available from a similar effect on Cβ–H bond breaking in the elimination of hydrogen bromide from β-haloethyl bromides [J. Hine and P. B. Langford, *J. Amer. Chem. Soc.*, **78**, 5002 (1956)]. For this system, ΔH^* for fluorine is about 12 kcal mol^{-1} larger than that for either chlorine or bromine.

and double-bond formation. These are generalized by the following equations.

$$ZC(NO_2)_2CH_2CH_2CN + OH^- \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}}$$
$$ZC(NO_2)_2\bar{C}HCH_2CN + H_2O \quad (10)$$

$$ZC(NO_2)_2\bar{C}HCH_2CN \overset{k_3}{\longrightarrow}$$
$$ZC(NO_2){=}CHCH_2CN + NO_2{}^- \quad (11)$$

Two limiting conditions exist: (1) $k_3 \gg k_{-1}$· [H$_2$O], nonreversible carbanion elimination, and (2) $k_3 \ll k_{-1}$ [H$_2$O], reversible carbanion elimination. It was possible to distinguish between the two by carrying out the reaction in a buffered deuterium oxide–dioxane solvent system.[25] After approximately one-third of **4**, Z = NO$_2$, had been converted to **7**, neither the recovered **4** nor the olefin **7** were found to contain deuterium. Therefore, $k_3 \gg k_{-1}$[H$_2$O] and every carbanion formed by β-proton abstraction loses nitrite to form the olefin **5** before it can be reprotonated to **4**.

The loss of the elements of nitrous acid from the substrates **4** by a nonreversible carbanion mechanism is reasonable in view of the structural factors present. Substituents such as ZC(NO$_2$)$_2$–, which have large σ^* values,[12,13] enhance the acidity of the β hydrogens, making them subject to facile removal by hydroxide. Stabilization of the resulting carbanion by the strong inductive effect slows down the rate of proton recombination. This rate retardation is coupled with the presence of a good leaving group, *i.e.*, nitro departing as resonance-stabilized nitrite ion. These factors combine to make $k_3 \gg k_{-1}$[H$_2$O] (eq 10, 11).

The use of fluorine labeling appears to be a useful tool for distinguishing between a concerted elimination reaction and a second-order carbanion elimination reaction. We are attempting to apply this technique to other systems to determine both the mechanism of the reaction and the position of the transition state along the reaction coordinate.

Experimental Section

Caution! Many of the compounds described in this work will detonate on grinding or impact. Extreme care should be taken when handling dry salts of the nitrocarbanions.

4,4,4-Trinitrobutyronitrile was prepared by adding 0.28 mol (15 g) of acrylonitrile to a solution of 0.265 mol (40 g) of trinitromethane in 125 ml of absolute ethanol. After standing for 24 hr at room temperature, the red-orange solution was poured into 500 ml of water and then extracted with three 100-ml portions of chloroform. The combined chloroform extracts were washed by percolating a stream of water through them until they were essentially colorless. The organic phase was dried over magnesium sulfate and concentrated *in vacuo* to about 100 ml. Pentane was added to the cloud point and the product crystallized on cooling in the freezer. It was rapidly filtered and dried with suction on the Buchner funnel. The solid melted at ambient temperature to an almost colorless liquid which was sufficiently pure for kinetic runs, as its nmr spectrum (CHCl$_3$–TMS) exhibited only a broad triplet, δ 3.47 (center), and a complex multiplet, δ 2.89 (center), of equal areas for the β-CH$_2$ and α-CH$_2$, respectively, yield 38 g (70%).

4,4-Dinitrobutyronitrile potassium salt was prepared from the trinitromethyl derivative and methanolic potassium iodide.[26]

4-Chloro-4,4-dinitrobutyronitrile was obtained by suspending 0.05 mol (9.85 g) of the potassium salt of 4,4-dinitrobutyronitrile

(25) J. Hine, R. Wiesboeck, and O. B. Ramsay, *J. Amer. Chem. Soc.*, **83**, 1222 (1961); J. Hine, R. Wiesboeck, and R. G. Ghirardelli, *ibid.*, **83**, 1219 (1961); L. R. Fedor, *ibid.*, **91**, 908 (1969).

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

in 50 ml of methylene chloride and passing dry chlorine through the suspension until the yellow color was discharged. The precipitated potassium chloride was removed by filtration and washed with 50 ml of methylene chloride, and the combined extracts were washed with 50 ml of saturated sodium bicarbonate (to remove dinitrobutyronitrile) and 100 ml of water and dried over magnesium sulfate. After the organic phase was treated with Darco G-60 charcoal, the solvent was removed *in vacuo.* The residual oil was flash distilled at 90° (0.1 mm) to yield 7.5 g (78%) of a pale yellow oil. *Anal.* Calcd for $C_4H_4ClN_3O_4$: C, 24.8; H, 2.1; N, 21.7; Cl, 18.3. Found: C, 24.9, 24.8; H, 2.0, 2.0; N, 20.3, 20.4; Cl, 18.2, 18.2.

4,4-Dinitro-4-fluorobutyronitrile was prepared by fluorinating a solution of 0.026 mol (5 g) of the potassium salt of 4,4-dinitrobutyronitrile in 200 ml of water containing 2.5 g of sodium bicarbonate with a stream of fluorine–nitrogen (1:3) until the yellow color of the solution was discharged. The turbid mixture was extracted with three 50-ml portions of methylene chloride. The combined extracts were washed with 5% sodium bicarbonate and then water and dried over magnesium sulfate. After the solvent was removed *in vacuo,* the residual oil was distilled at 70° (0.3 mm) to yield 3.6 g (78%) of a colorless oil. *Anal.* Calcd for $C_4H_4FN_3O_4$: C, 27.1; H, 2.3; N, 23.7; mol wt, 177. Found: C, 27.1, 27.5; H, 2.4, 2.5; N, 22.9, 22.3; mol wt, 174, 178 (osmometer).

4-Chloro-4,4-dinitrobutyric acid and 4,4-dinitro-4-fluorobutyric acid were prepared as described previously.[12]

4-Fluoro-4-nitro-2-butenoic acid dipotassium salt was prepared by adding a solution of 0.02 mol (3.92 g) of 4,4-dinitro-4-fluorobutyric acid in 20 ml of methanol to a solution of 0.1 mol (5.6 g) of potassium hydroxide in 50 ml of methanol. After 1 hr, the salt was collected by filtration, washed twice with 10-ml portions of methanol and once with 10 ml of ether, and air dried. The pink salt, 2.66 g (60%), could not be recrystallized without extensive decomposition and was therefore analyzed directly. *Anal.* Calcd for $K_2C_4H_2FNO_4$: K, 34.7; C, 21.3; H, 0.89; N, 6.2. Found: K, 33.8; C, 21.4; H, 1.1; N, 6.6.

4-Chloro-4-nitro-2-butenoic acid dipotassium salt was prepared by adding a solution of 0.01 mol (2.12 g) of 4-chloro-4,4-dinitrobutyric acid in 10 ml of ether to a solution of 0.05 mol (2.8 g) of potassium hydroxide in 20 ml of methanol. There was an almost immediate precipitation of an amorphous orange salt. The product could not be recrystallized, and, after it was washed with 50% ether in methanol, its ultraviolet spectrum, λ_{max} 322 nm (ϵ 12,400), indicated that the salt was not pure, as the value of the molar extinction coefficient seemed low. However, no impurities were detected in its nmr spectrum (Table III). Therefore, the contaminants were assumed to be inorganic.

The proof of a single reaction path and a good value of the molar extinction coefficient were obtained by the following procedure in which a mole for mole correspondence between the nitrite ion and 4-chloro-4,4-dinitrobutyric acid concentrations were obtained. A sample of 1.006×10^{-4} mol (0.021384 g) of 4-chloro-4,4-dinitrobutyric acid was rinsed into a 100-ml volumetric flask with 5 ml of methanol and 25 ml of water added. Then 5 ml of 20 *M* sodium hydroxide was introduced, and the solution was mixed thoroughly and allowed to stand for 30 min. After it was diluted to volume with water, a 6-ml aliquot was diluted to 100 ml with water. The ultraviolet spectrum of this solution exhibited λ_{max} 322 nm (ϵ 16,400), $OD_{322} = 0.990$. Analysis of this dilution for nitrite[14] gave $10^5[NO_2^-] = 6.01$. For a quantitative conversion of the 4-chloro-4,4-dinitrobutyric acid originally present in this dilution $10^5[NO_2^-] = 6.04$. No chloride ion could be detected in this reaction mixture.

4-Chloro- and 4-Fluoro-4-nitro-2-butenenitrile Potassium Salt. —On a synthetic scale, it was not possible to isolate these products, as they were apparently unstable out of solution. Molar extinction coefficients and proof of a single reaction path for their formation were determined in the following manner. A solution of 1.26×10^{-4} mol (0.024613 g) of 4-chloro-4,4-dinitrobutyronitrile in 5 ml of methanol in a 100-ml volumetric flask was diluted to volume with 0.1 *M* sodium hydroxide. Samples were withdrawn at intervals and appropriately diluted with water, and the absorbance was measured at 342 nm. After about 45

min, the value of the absorbance was constant and 6 ml of the reaction mixture was diluted to 100 ml with water. The spectrum of this dilution showed λ_{max} 342 mm (ϵ 13,800), $OD = 1.043$. Nitrite ion was equal to 7.74×10^{-5} *M* as compared with 7.56×10^{-5} *M* 4-chloro-4,4-dinitrobutyronitrile originally present in this dilution.

For 4,4-dinitro-4-fluorobutyronitrile, using 0.2 *M* sodium hydroxide as the reaction medium, $10^5[FC(NO_2)_2CH_2CH_2CN] = 4.00, 10^5 [NO_2^-] = 4.12$, λ_{max} 335 nm (ϵ 23,000), $OD = 0.920$.

Reaction of 4,4,4-Trinitrobutyronitrile with Hydroxide in Dioxane–D₂O.—To a solution of 0.05 mol (5 g) of potassium bicarbonate in 70 ml of D₂O and 55 ml of purified dioxane[14] was added 0.01 mol (2.04 g) of 4,4,4-trinitrobutyronitrile. The course of the reaction was followed spectrophotometrically and after 35 min, 36% of the trinitro species had reacted. The mixture was extracted with four 20-ml portions of methylene chloride. The combined extracts were washed with 20 ml of D₂O and dried over magnesium sulfate, and the solvent was removed *in vacuo.* The residual oil was analyzed for deuterium by comparing the integral at δ 3.47 for β-CH₂ (29.8 ± 0.7) with the integral at δ 2.89 for α-CH₂ (29.5 ± 0.3) in the recovered starting material.

The elimination product 7 was isolated by concentrating the aqueous phase under reduced pressure (60°) till the orange potassium salt separated from solution. The product was collected on a Buchner, washed with methanol and then ether, and dried. The integrals of the two doublets for the olefinic protons at δ_{H_β} 7.75 and 7.91 and δ_{H_α} 5.86 and 6.02 (DMSO–TMS) were 61.0 ± 0.0 and 61.0 ± 0.7. Therefore, no deuterium was picked up from the solvent during the reaction.

Reaction of 4,4,4-Trinitrobutyronitrile with Hydroxide and Thiosulfate in Dioxane–D₂O.—The procedure described above was followed except that 0.05 mol (12.4 g) of sodium thiosulfate pentahydrate was dissolved in the reaction medium prior to the addition of the trinitro substrate. The course of the reaction was followed spectrophotometrically on diluted aliquots and after 3 hr at 50° essentially all of the first formed thiosulfate ester 9, λ_{max} 368 nm, was converted to the olefin 9. The reaction mixture was concentrated *in vacuo* (60°) till crystallization just started. After cooling in ice water, the salt was collected on a Buchner funnel, washed with methanol and then ether, and dried. Integrals of the two doublets for the olefinic protons in the nmr spectrum of 7 (DMSO–TMS) were equal to 68.3 ± 0.3 and 69.0 ± 0.7 for CHβ and CHα, respectively.

General Kinetic Procedure.—Appropriate aliquots of stock solutions of the buffer components, added salt, and when necessary sodium thiosulfate were added to a 100-ml volumetric flask. Distilled water was added to a volume of about 90 ml and the resulting solution was thermostated at the desired temperature for 30 min. To this solution was added an aliquot (5 ml or smaller) of the thermostated nitro substrate stock solution (about 1–5 × 10^{-3} *M*) in 5% aqueous methanol. The mixture was made up to volume with thermostated distilled water and mixed by shaking, and a sample was transferred to a thermostated cell in a Cary Model 14 spectrophotometer. This procedure generally took about 1 min. The increase in absorbance at λ_{max} for the product (Table II) was followed with time. The pH measurements were made on a thermostated sample of the reaction mixture with either a Beckman Model G or Research pH meter. Rate constants were calculated from these data as described in the Results and Discussion section.