Influence of Solvent and Counterion in the Reactions of Alkoxide Ions with the 2-Nitropropan-2-yl Radical

Glen A. Russell* and Woonphil Baik

Department of Chemistry, Iowa State University, Ames, Iowa 50011, U.S.A.

Photostimulated free radical chain reactions between alkoxide ions derived from primary alcohols and $XCMe_2NO_2$ (X = Cl, Br, NO_2, $PhSO_2$, N_3, or *p*-ClC_6H_4S) occur to produce $Me_2C(OR)_2$ by a reaction involving the trapping of $Me_2C(NO_2)\cdot$ by RO^-, the decomposition of $ROCMe_2NO_2\cdot^-$ to $ROCMe_2\cdot$, and the oxidation of $ROCMe_2\cdot$ to $Me_2C{=}OR^+$ by $XCMe_2NO_2$.

Carbon-, sulphur-, and phosphorus-centred nucleophiles are known to participate in photostimulated $S_{RN}1$ chain reactions with α-substituted nitroalkanes (*e.g.* $XCMe_2NO_2$ with X = Cl, Br, NO_2, SO_2Ph, SAr, N_3) in which $Me_2C(NO_2)\cdot$ is trapped by the nucleophile to yield the radical ion of the substitution product.[1,2] However, oxygen-centred nucleophiles are generally considered to be unreactive in such processes. We have found that alkoxide ions derived from primary alcohols will trap $Me_2C(NO_2)\cdot$ but that the resulting $Me_2C(NO_2)OR\cdot^-$ undergoes fragmentation into $Me_2C(OR)\cdot$ and NO_2^-. Thus, photostimulated reaction (1) occurs with R = Me, Et, Bu^n, 2-methoxyethyl, or allyl, and with X = Cl, Br, NO_2, $PhSO_2$, N_3, or *p*-ClC_6H_4S (Table 1). Similar reactions occur for $MeCCl_2NO_2$, $PhC(Br)(SO_2Ph)NO_2$, and cyclo-$C_3H_5C(Me)(Cl)NO_2$ to yield $MeC(OMe)_3$ (56%), $PhC(OMe)_3$ (48%), and cyclo-$C_3H_5C(Me)(OMe)_2$ (68%), respectively.

The reactions do not occur in the dark or in the presence of oxygen and can be inhibited for discrete periods of time by $(Bu^t)_2NO\cdot$, see Figure 1.[†] The rate of disappearance of

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[†] Measured initial kinetic chain lengths (k.c.l.) (initial reaction rate/rate of initiation) were greater in EtOH than MeOH and greater for K^+ than Na^+. With 0.1 M-$BrCMe_2NO_2$ and 0.2 M-ROM, the measured k.c.l. were NaOMe (10); KOMe (75); NaOEt (38); KOEt, (171). Initiation rates were approximately the same with K^+ and Na^+, but were greater in MeOH than in EtOH.

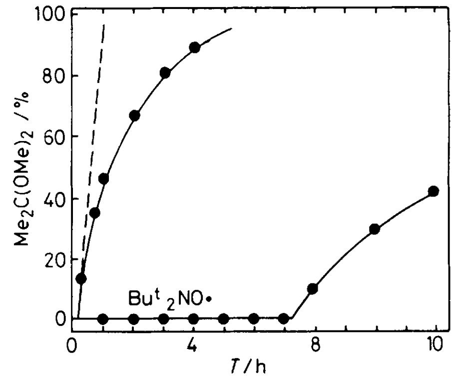


Figure 1. Photostimulated reaction of $BrCMe_2NO_2$ (0.10 M) with MeOK (0.20 M) in MeOH in the absence and presence of $Bu^t{}_2NO\cdot$ (0.010 M). The two experiments were performed under the same irradiation conditions at 350 nm in a Rayonet Photoreactor at 35 °C.

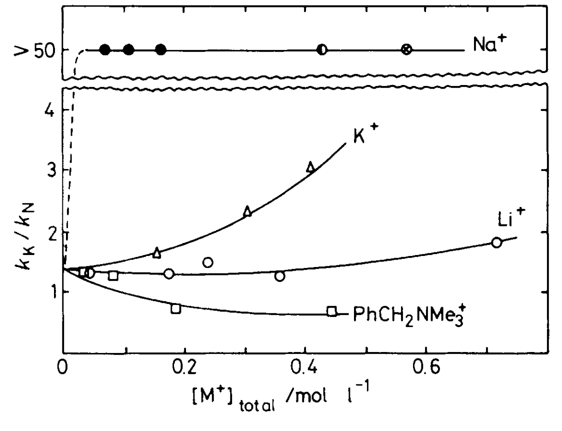


Figure 2. Photostimulated reaction of $BrCMe_2NO_2$ with MeO^- and $Me_2C=NO_2^-$ in MeOH at 35 °C: ○, ●, △, □, ⊗, $[MeO^-M^+]_0 = [Me_2C=NO_2^-M^+]_0 \approx 1.5\,[BrCMe_2NO_2]_0$; ◐, $[MeO^-M^+]_0 = [Me_2C=NO_2^-M^+]_0 = 3\,[BrCMe_2NO_2]_0$; ⊗, 0.42 M-$NaClO_4$ added.

$XCMe_2NO_2$ is equal to the rate of appearance of $Me_2C(OMe)_2$, and no intermediate, such as the unknown $MeOCMe_2NO_2$, can be detected by ^1H n.m.r. in CD_3OD. The yield of the ketal is greatly reduced by the presence of $Me_2C=NO_2M$ (M = Li, K, $PhCH_2NMe_3$) or 4 equivalents of an electron-rich alkene such as $CH_2=C(OMe)Ar$ (Ar = Ph, p-$MeOC_6H_4$). These observations are consistent with a free radical chain mechanism (reactions 2—5) in which the neutral

$$2\,RO^- + XCMe_2NO_2 \xrightarrow[ROH]{h\nu} Me_2C(OR)_2 + X^- + NO_2^- \quad (1)$$

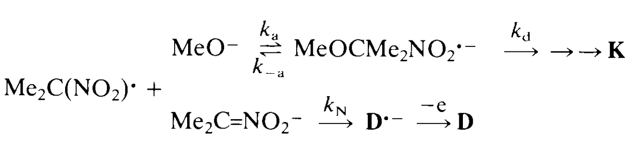
$$XCMe_2NO_2\cdot^- \longrightarrow Me_2C(NO_2)\cdot + X^- \quad (2)$$

$$Me_2C(NO_2)\cdot + RO^- \longrightarrow ROCMe_2NO_2\cdot^- \quad (3)$$

$$ROCMe_2NO_2\cdot^- \longrightarrow ROCMe_2\cdot + NO_2^- \quad (4)$$

$$ROCMe_2\cdot + XCMe_2NO_2 \longrightarrow Me_2C=OR^+ + XCMe_2NO_2\cdot^- \quad (5)$$

radical $ROCMe_2\cdot$ is oxidized to the cation by $XCMe_2NO_2$.‡ The presence of the alkoxy substituent undoubtedly provides a driving force for both reactions (4) and (5) by stabilization of $ROCMe_2\cdot$ and $Me_2C=OR^+$.



$$Me_2C(NO_2)\cdot + \begin{cases} MeO^- \underset{k_{-a}}{\overset{k_a}{\rightleftharpoons}} MeOCMe_2NO_2\cdot^- \xrightarrow{k_d} \rightarrow\rightarrow \mathbf{K} \\ Me_2C=NO_2^- \xrightarrow{k_N} \mathbf{D}\cdot^- \xrightarrow{-e} \mathbf{D} \end{cases}$$

Scheme 1

Table 1. Photostimulated reactions of $Me_2C(NO_2)X$ with MeONa–MeOH[a]

X	T/h	Yield of $Me_2C(OR)_2$/%
Br	5 (dark)	0
Br	5	96
NO_2	12	84
$PhSO_2$	5	82
N_3	24	74
p-ClC_6H_4S	2	11

[a] $[Me_2C(NO_2)X]_0$ 0.1 M, $[MeONa]_0$ 0.2 M. Reactions were irradiated in a Rayonet Photoreactor (350 nm) at 40 °C.

Competition between MeOK and $Me_2C=NO_2K$ for $Me_2C(NO_2)\cdot$ yields mixtures of $O_2NCMe_2CMe_2NO_2$ (**D**) and $Me_2C(OMe)_2$ (**K**) in MeOH but only **D** in Me_2SO. The ratio **K** : **D** is consistent with Scheme 1 in which ion pairing and/or hydrogen bonding favours the formation of the ketal. The relative reactivity of MeO^- and $Me_2C=NO_2^-$ towards $Me_2C(NO_2)\cdot$ was evaluated from the product yields by the rate expression $k_K/k_N = \log([MeO^-]_f/[MeO^-]_0/2\log([Me_2C=NO_2^-]_f/[Me_2C=NO_2^-]_0)$, where $[MeO^-]_f = [MeO^-]_0 - 2[\mathbf{K}]$, $[Me_2C=NO_2^-]_f = [Me_2C=NO_2^-]_0 - [\mathbf{D}]$, and $k_K = k_a k_d/(k_{-a} + k_d)$. With K^+ as the counterion, the relative reactivity thus measured was independent of $[BrCMe_2NO_2]_0$, the extent of the reaction, of the initial ratio of the nucleophiles (Figure 2). While some variation in k_K/k_N is observed, the effect of the concentration of K^+, Li^+ or $PhCH_2NMe_3^+$ upon the relative reactivity is not particularly important in MeOH ($k_K/k_N = 2 \pm 1$). However, with Na^+ in MeOH the relative reactivity is 50 : 1 (no **D** observed). Apparently, specific ion pairing effects with Na^+ in MeOH greatly lowers the reactivity of $Me_2C=NO_2^-$ relative to MeO^-.§

Electron-rich alkenes, such as $CH_2=C(OMe)Ar$, will trap $Me_2C(NO_2)\cdot$ as shown by a greatly decreased yield of **K** or **D** in competitive reactions with NaOMe, KOMe, or $Me_2C=NO_2K$. These observations exclude the formation of $MeOCMe_2NO_2\cdot^-$ by an $S_{RN}2$ process ($BrCMe_2NO_2\cdot^-$ + MeO^-) not involving the formation of free $Me_2C(NO_2)\cdot$.[5]

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‡ In radiolytic processes, $R\dot{C}HOH$ and $R\dot{C}HOR'$ are oxidized by nitrobenzene or $C(NO_2)_4$ *via* the formation of a nitroxide intermediate.[3]

§ In the competition between nucleophiles for $Me_2C(NO_2)\cdot$, preferential ion-pairing with Li^+ in Me_2SO causes a considerable decrease in the reactivities of $RC(CO_2Et)_2^-$ and $(EtO)_2PO^-$ relative to $Me_2C=NO_2^-$.[4]

However, in the presence of enol ethers there was no evidence of product formation *via* electron transfer from the expected adduct radicals ($O_2NCMe_2CH_2\dot{C}(OMe)Ar$). Thus, the possibility exists that $MeOCMe_2NO_2$ (from electron transfer between $MeOCMe_2NO_2^{\bullet -}$ and $BrCMe_2NO_2$) might be an intermediate in reaction (1) provided it is rapidly converted into $Me_2C(OMe)_2^{\bullet}$. However, for p-$ClC_6H_4SCMe_2NO_2$,[6] a reasonable model for $MeOCMe_2NO_2$, nitrite ion displacement was not seen to occur in the dark, while u.v. photolysis gave only a low yield of $Me_2C(OMe)_2$ (Table 1). Instead, with p-$ClC_6H_4SCMe_2NO_2$ in CD_3ONa–CD_3OD a slow dark reaction, unaffected by $Bu^t_2NO^{\bullet}$, yielded p-$ClC_6H_4S^-$ and $Me_2C{=}NO_2^-$, presumably with the oxidation of methoxide ion.¶

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¶ Reactions of $XCMe_2NO_2$ with ArS^- do not form $Me_2C(SAr)_2$. $Me_2C(SAr)NO_2^{\bullet -}$ in H_2O–MeOH, Me_2SO, or dimethylformamide undergoes electron transfer to $XCMe_2NO_2$ or decomposes to either ArS^- and $Me_2C(NO_2)^{\bullet}$ or $ArS^{\bullet}$ and $Me_2C{=}NO_2^-$.[7]