

mode of dispersal of platinum on the semiconductor particle, and of the optimum geometry in the integrated system on the efficiency of gas evolution.

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One-Electron Reduction of Nitrobenzenes by α -Hydroxyalkyl Radicals via Addition/Elimination. An Example of an Organic Inner-Sphere Electron-Transfer Reaction

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Abstract: The reactions in aqueous solution of α -hydroxyalkyl radicals with para-substituted nitrobenzenes were studied by using product analysis, electron spin resonance, and pulse radiolysis techniques. At neutral pH the α -hydroxyalkyl radicals are quantitatively oxidized to yield the corresponding ketones or aldehydes and H⁺, and the nitrobenzenes are reduced to the radical anions. The mechanism of this redox reaction depends strongly on the substituents on the α -hydroxyalkyl radical (the electron donor) and on the nitrobenzene (the electron acceptor). In the case of α -hydroxymethyl radical, the reaction proceeds by addition to the nitro group to produce an alkoxy nitroxyl radical which can undergo an OH⁻-catalyzed heterolysis to give formaldehyde and the radical anion of the nitrobenzene. With the α -hydroxyethyl radical, both addition and "electron transfer" take place, the fraction of electron transfer increasing with increasing electron-withdrawing power of the substituent. The nitroxyl-type adducts undergo a spontaneous unimolecular heterolysis to give acetaldehyde, H⁺, and nitrobenzene radical anion. The rate constants k_1 (from $<10^2$ to 5×10^4 s⁻¹) for this heterolysis increase with increasing electron-withdrawing strength of the substituent if it is on the benzene, and they decrease if the substituent is on the methyl carbon of the nitroxyl. The heterolysis reaction is characterized by low (5–10 kcal/mol) activation enthalpies and strongly negative (–5 to –25 eu) activation entropies, which originate from hydration of a proton in the transition state. From the effect on the activation parameters exerted by substituents on the electron acceptor and on the electron donor parts of the nitroxyl radical it is concluded that the heterolysis reaction proceeds by a push-pull mechanism and is entropy controlled. In the reaction of the α -hydroxyprop-2-yl radical with substituted nitrobenzenes, the lifetimes of potential adducts of the nitroxyl type are ≤ 1 μ s if the substituent R is less electron donating than OH. However, if R = NH₂, an adduct is formed which undergoes spontaneous heterolysis with $k_1 = 2.1 \times 10^3$ s⁻¹. The heterolysis reaction can also be slowed down by making the solvent less polar than water: in 95% propan-2-ol/5% water $k_1 = 1.5 \times 10^4$ s⁻¹ for R = CN as compared to $>10^6$ s⁻¹ in water.

The one-electron reduction of nitro compounds has received considerable attention, particularly as a result of the interest in structure-reactivity correlations concerning radicals² and also in view of the application of nitro aromatics as radiosensitizers in radiotherapy.³ In order to reduce the nitro compounds, these have often been reacted with α -hydroxyalkyl radicals, which generally behave as potent one-electron donors.² However, as shown⁴ as early as 1968 by ESR measurements, the mechanism of interaction of α -hydroxyalkyl radicals and nitro compounds is more complicated than expected on the basis of simple electron transfer between the reactants. Depending on the nature of the

α -hydroxyalkyl radical and on solvent or pH, nitroxide-type radicals, formed by addition rather than electron transfer, were detected.^{4,5} These observations were supported by the results of pulse radiolysis experiments using optical detection,⁶ and it was concluded^{4,6} that it is the stability of the conjugate carbonium ions⁷ that determines whether the reaction between an α -hydroxyalkyl radical and the nitro compound proceeds by electron transfer or by addition. On the other hand, it has been pointed out⁸ also that the redox potential of the nitro compound may determine the probability of radical addition or electron transfer. However, the dependence of the reaction pattern on the structure of the reactants has not been systematically studied. Furthermore, the potential influence of solvent and of pH has not received the necessary attention, although it was demonstrated⁴ already in 1968 that, e.g., the adduct of the hydroxymethyl radical to nitrobenzene

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undergoes an OH⁻-catalyzed decomposition to yield the nitrobenzene radical anion.

We have recently shown⁹ that the one-electron oxidation of α -alkoxyalkyl radicals by the nitro compound tetranitromethane proceeds by an addition/elimination sequence and that the unimolecular heterolysis of the adducts is extremely sensitive to variations in the electron-donor properties of the α -alkoxyalkyl radicals. In that work⁹ the electron acceptor (tetranitromethane) was not varied. The present work is a systematic study of the consequences of varying (a) the strengths of both electron donor and acceptor in the reaction between α -hydroxyalkyl radicals and substituted nitrobenzenes and (b) of changing solvent, pH, and temperature.

The results demonstrate the existence of strongly polar structures of the transition states in the electron-transfer sequence that proceeds via formation and decomposition of adducts. As a result entropic factors related to considerable solvent reorganization in the transition state are of great importance.

Experimental Section

The nitro compounds (purity $\geq 98\%$) were obtained from Aldrich, Bader, Eastman, Fluka, or Pfaltz and Bauer and were used as received. Analytical grade methanol, ethanol, 1- and 2-propanol, ethylene glycol, and sodium formate were from Merck. The purity of the other alcohols used was $\geq 98\%$. The solutions typically contained 0.1–2 M alcohol and 0.1–2 mM nitro compound in water that was triply distilled: from alkaline permanganate, from acid dichromate, and finally from a quartz vessel. The solutions were saturated with N₂O in order to convert e_{aq}⁻ into OH, and they were irradiated with 3-MeV electron pulses of 0.1–0.4 μ s duration with doses such that 0.2–1 μ M radicals were produced. The optical transmission or conductance signals from the thermostatable detection cells¹⁰ (temperature constancy ± 0.02 °C) were digitized with use of a Biomation 8100 transient recorder and fed into a PDP11/10 minicomputer connected to a VAX11/780 computer, which was used for the storage, processing, and analysis of the experimental data.

For the optical experiments, dosimetry was performed with N₂O-saturated 10 mM KSCN solutions taking $\epsilon\{(\text{SCN})_2^-\}$ at 480 nm = 7600 M⁻¹ cm⁻¹ and $G(\text{OH}) = 6.0$.¹¹ Extinction coefficients of the substituted nitrobenzene radical anions were determined by using N₂O-saturated 0.1 M sodium formate solutions containing 0.2–0.5 mM nitrobenzene and taking $G(\text{radical anion}) = G(\text{CO}_2^-) = G(\text{OH} + \text{H}) = 6.6$. For experiments with conductance detection, two dosimetry methods were applied: (a) 0.1 M methanol with 0.2–0.5 mM tetranitromethane at pH 4–5, for which $G(\text{H}^+) = G(\text{CH}_2\text{OH}) = G(\text{OH} + \text{H}) = 6.6$, and (b) 0.1 M *tert*-butyl alcohol saturated with CH₃Cl, for which $G(\text{H}^+) = G(\text{e}_{\text{aq}}^-) = 3.14$.¹² Methods a and b agreed within 10%.

Electron spin resonance spectra were recorded by using the in-situ-radiolysis-ESR method.¹³

For product analysis studied, ⁶⁰Co- γ -irradiated solutions containing a nitrobenzene and methanol, ethanol, or 2-propanol were analyzed for CH₂O by the Hantzsch method,¹⁴ or for CH₃CHO or (CH₃)₂CO by GC. Samples (5 μ L) of the aqueous solutions, which contained 0.01–0.1 mM isobutyl alcohol as an internal standard, were injected directly into a modified¹⁵ Varian 1400 instrument with flame ionization detection. The split ratio was 1:40. A 52-m glass capillary column coated with OV1 ("thick film") was used at 70 °C. The carrier gas was N₂. Retention times were ≤ 10 min, and the detection limit corresponded to ≈ 5 μ M acetaldehyde or acetone.

Results

(1) Reactions of $\dot{\text{C}}\text{H}_2\text{OH}$. (a) **Acid Solutions (pH 3–6).** The reactions of $\dot{\text{C}}\text{H}_2\text{OH}$ with the nitrobenzenes were investigated by using in-situ-radiolysis-ESR spectroscopy and product-analysis methods and also time-resolved optical and conductance detection

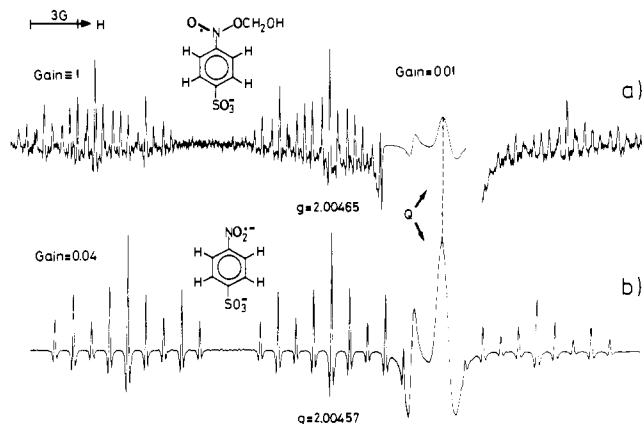


Figure 1. ESR spectra of radicals produced by the reaction of $\dot{\text{C}}\text{H}_2\text{OH}$ with 4-nitrobenzenesulfonate (1 mM) at 5 °C. [CH₃OH] = 0.2 M: (a) pH 4.1, (b) pH 8.6. Q symbolizes the signal from the quartz cell.

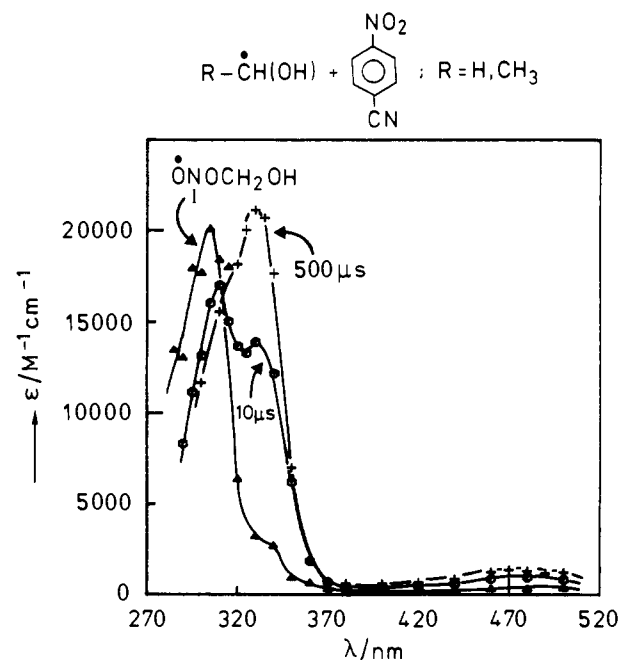
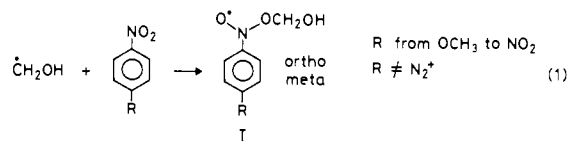


Figure 2. Optical absorption spectra observed on reaction of $\dot{\text{C}}\text{H}_2\text{OH}$ (triangles) and $\text{CH}_3\dot{\text{C}}\text{HOH}$ (circles and crosses) with 1 mM 4-nitrobenzonitrile at pH 4–5 and 20 °C: circles, spectrum measured 10 μ s after initiation of the reaction, i.e., after quantitative scavenging of $\text{CH}_3\dot{\text{C}}\text{HOH}$; crosses, spectrum observed at 500 μ s, i.e., after completion of the heterolysis reaction, eq 6S.

techniques. $\dot{\text{C}}\text{H}_2\text{OH}$ was produced by H abstraction from methanol by the OH (and H) radicals generated by irradiation of N₂O-saturated aqueous solutions containing 0.1–2 M methanol. On addition of 0.1–1 mM para-substituted nitrobenzenes to the solutions, at pH 3–6 nitroxide-type radicals were produced, as shown by in-situ-radiolysis-ESR experiments (Figure 1a). The nitroxide radicals are formed by addition of $\dot{\text{C}}\text{H}_2\text{OH}$ to the nitro group⁴ (eq 1). Nitrobenzene radical anions were not detected.



The ESR spectra (Figure 1a) of the nitroxide radicals (=adducts) are all characterized by the presence of a ¹⁴N splitting (coupling constants between 13.8 and 16.7 G) and three sets of two equivalent protons with splittings of ~ 3 , ~ 1 , and ~ 0.5 G, respectively, which are assigned to the protons ortho and meta to the nitroxide group and to those at CH₂OH. The results are summarized in Table I, which also contains the ESR parameters

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Table I. Coupling Constants (Gauss) and *g* Factors of Nitroxide and Anion Radicals of Para-Substituted Nitrobenzenes

substituent	NO ₂ ^{-a}				Δ <i>a</i> (N)	N(O)OCH ₂ OH ^b				<i>g</i> (anion)	<i>g</i> (nitroxide)	notes	
	<i>a</i> _o ^c	<i>a</i> _m	<i>a</i> _p	<i>a</i> (N)		<i>a</i> (N)	<i>a</i> _o ^c	<i>a</i> _m	<i>a</i> _{CH₂}				
SO ₃ CH ₃	3.32	1.03		11.75	2.06	13.81	3.15		1.05	0.45	2.00461	2.00481	from ref 28b
NO ₂	1.09 (4)			4.66 (2)							2.00485		
CN	3.35	1.12	0.57 ^d	11.79	2.02	13.81	3.15		1.15	0.45 ^e	2.00463	2.00469	
SO ₂ NH ₂	3.36	1.10	0.13 ^f	12.27	2.08	14.35					2.00452	2.00466	
CHO	3.44, 2.98	1.02	0.60 ^g	11.13							2.00484		
CF ₃	3.40	1.13	5.51 ^h	12.92							2.00455		
COCH ₃	3.28	1.09	0.41 ⁱ	11.70	2.17	13.87					2.00470	2.00480	
CO ₂ H	3.32	1.12		12.22	1.99	14.21	3.16		1.11	0.46	2.00479	2.00473	
CO ₂ CH ₃	3.33	1.12	0.26 ^k	12.21	1.95	14.16					2.00471	2.00474	
SO ₃ ⁻	3.38	1.14		12.81	1.99	14.80	3.17		1.10	0.45	2.00457	2.00465	
CONH ₂	3.34	1.12	0.24 ^l	12.49							2.00464		
Cl	3.44	1.20	0.26 ^m	13.75							2.00490		
CO ₂ ⁻	3.35	1.14		13.02	1.86	14.88	3.20		1.12	0.48	2.00458	2.00472	
CH=NOH	3.45	1.28	<i>n</i>	12.90							2.00486		
F	3.48	1.15	8.19 ^o	14.48							2.00472		
CH ₂ OH	3.36	1.13	2.51 ^p	14.02							2.00453		
H	3.38	1.15	3.65	14.20	1.80	16.0 ^q	3.22 ^q		1.14 ^q	0.57 ^q	2.00448		<i>r</i>
CH ₃	3.39	1.13	3.82 ^s	14.45	1.87	16.32	3.23 (3.12 ^t)		1.10	0.53	2.00442	2.00455	<i>t</i>
OCH ₃	3.42	1.06	0.39 ^u	14.82	1.84	16.66					2.00460	2.00457	
OH	3.41	1.07		14.95							2.00460		
NH ₂	3.35	1.15		14.90							2.00441		from ref 29
O ⁻	3.26	0.82		15.53							2.00460		

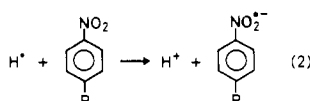
^a Measured using aqueous solutions that contained ~0.1 M formate, methanol, ethanol, or propan-2-ol and 0.2–1 mM nitrobenzene, pH 8–10. The temperature was ~5 °C. ^b [Methanol] = 1 M, 1 mM nitrobenzene, pH 4–5, 5 °C. ^c The ring positions are assigned relative to the nitro group. ^d *a*(N)_{CN}. ^e *a*(N)_{CN} is also 0.45 G. ^f *a*(N)_{SO₂NH₂}. ^g *a*(H)_{CHO}. Note: the ortho protons are not equivalent. ^h *a*(F)_{CF₃}. ⁱ *a*(H)_{COCH₃}. ^k *a*(H)_{COOCH₃}. ^l *a*(N)_{CONH₂}. ^m *a*(Cl). ⁿ pH 11.2; the aldoxime group is probably ionized; *a*(H)_{CH=NO⁻} = 1.28 G, *a*(N)_{CH=NO⁻} = 1.56 G. ^o *a*(F). ^p Refers to the benzyl protons. ^q From ref 4. ^r Radical anion data from ref 13. ^s *a*(H)_{CH₃}. ^t Radical anion data from ref 29. ^u *a*(H)_{OCH₃}.

of the corresponding radical anions. There is a correlation between the Hammett σ values of the substituents and the coupling constants for ¹⁴N: for both the adducts and the radical anions *a*(¹⁴N) decreases with increasing σ .

Experiments were also carried out using optical detection. On producing $\dot{\text{C}}\text{H}_2\text{OH}$ by pulse irradiation of (N₂O saturated) aqueous solutions containing methanol in the presence of substituted nitrobenzenes, transients absorbing at 280–310 are formed (Figure 2). The transients are identified as the nitroxide radicals I (eq 1). The rates of the exponential buildup of optical density increased linearly with increasing concentration of nitro compound, and from these dependencies the rate constants for formation of the nitroxide-type radicals were obtained. As seen from Table II, the rate constants are of the order 10⁷–10⁸ M⁻¹ s⁻¹. Where comparison is possible, it is seen that the absorption maxima and extinction coefficients of the nitroxide radicals are similar to those^{16,17} of the corresponding protonated radical anions, i.e., the effect of alkylation (by HOCH₂⁺) of the radical anion is comparable to that of its protonation.

At pH ≤ 6 the nitroxide radicals decay by predominantly second-order kinetics ($2k \approx 10^8$ – 10^9 M⁻¹ s⁻¹).

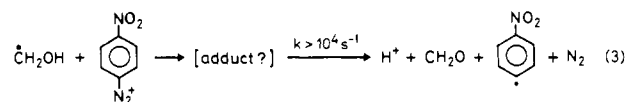
In order to further test whether ions are formed in the reaction of HOCH₂ with the nitrobenzenes at pH 3–6, experiments with conductivity detection were performed. With all the substituted benzenes from R = NH₂ to R = NO₂, only very small signals were observed in the time range ≤ 10 ms after initiation of reaction 1. These signals can be explained exclusively by the reaction of (a) that portion of the small (<10% of the OH radicals) concentration of H atoms (produced by irradiation of the aqueous solutions) that did not react with methanol but via eq 2 and (b) by that fraction of e_{aq}⁻ that did react with the nitrobenzenes rather than with N₂O. The absence of conductance signals from the reaction



of HOCH₂ at pH 3–6 is in support of the results from ESR and

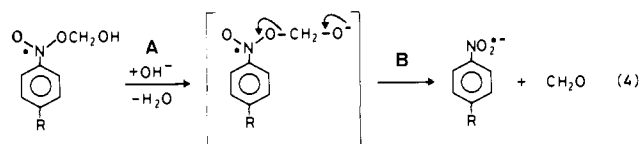
optical measurements which showed that nitrobenzene radical anions are not produced.

4-Nitrobenzenediazonium tetrafluoroborate (R = N₂⁺) was the only nitrobenzene to give ions from the reaction of HOCH₂. This reaction (eq 3) has been shown to initiate a chain reaction with the 4-nitrophenyl radical as the chain carrier.^{18a}



In the reaction of $\dot{\text{C}}\text{H}_2\text{OH}$ with the nitrobenzenes, formaldehyde is one of the stable products. Under conditions of low production rates of radicals such as in γ -radiolysis, the yield per $\dot{\text{C}}\text{H}_2\text{OH}$ of CH₂O was found to be unity at pH ≥ 6 and only 10% less at pH ≈ 4. This shows that the nitroxide radicals formed according to eq 1 under these conditions give rise essentially quantitatively to formaldehyde, i.e., the nitrobenzenes oxidize $\dot{\text{C}}\text{H}_2\text{OH}$ by removal of one electron.^{18b}

(b) **Solutions of pH > 6.** Figure 1b shows the ESR spectrum recorded on the reaction of $\dot{\text{C}}\text{H}_2\text{OH}$ with 4-nitrobenzenesulfonate at pH 8.6. The spectrum, which does not change between pH 7 and 13, is due to the radical anion of the nitro compound. The radical can be produced also at pH < 7 by reaction with, e.g., e_{aq}⁻, CO₂⁻, (CH₃)₂COH, or CH₃CHOH. At pH 6–7 the nitroxide type radical I (R = SO₃⁻) and the radical anion can be observed simultaneously. Since in the pH range 6–9 neither nitrobenzenesulfonate nor $\dot{\text{C}}\text{H}_2\text{OH}$ change their dissociation state, the formation of radical anion must be due to reaction of I (R = SO₃⁻) with OH⁻, cf.



The exclusive formation of radical anions on reaction of $\dot{\text{C}}\text{H}_2\text{OH}$ at pH > 7 was observed also with other substituted nitrobenzenes. The ESR parameters taken from the experimental spectra are

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Table II. Rate Constants for Reaction of Para-Substituted Nitrobenzenes with α -Hydroxyalkyl^a Radicals and CO₂⁻

substituent R	$k_R, M^{-1} s^{-1}$			
	$\dot{C}H_2OH^b$	$CH_3\dot{C}HOH^{b,d}$	$(CH_3)_2\dot{C}OH^d$	CO ₂ ^{-d,e}
SO ₃ CH ₃	1.2×10^8	1.3×10^9 $1.3 \times 10^9^c$	2.4×10^9	1.5×10^9
NO ₂	2.0×10^8	2.4×10^9 $2.3 \times 10^9^c$	$3.2 \times 10^9^f$	2.1×10^9
CN	1.0×10^8	1.2×10^9 $9.4 \times 10^8^c$	2.7×10^9	2.1×10^9
SO ₂ NH ₂	8.6×10^7	7.9×10^8 $7.8 \times 10^8^c$	2.3×10^9	1.1×10^9
CHO	9.1×10^7	1.8×10^9 $1.5 \times 10^9^c$	2.8×10^9	2.6×10^9
CF ₃		$4.3 \times 10^8^c$	1.9×10^9	$\sim 1 \times 10^9$
COCH ₃	8.6×10^7	1.0×10^9 $9.2 \times 10^8^c$	1.5×10^9 $2.0 \times 10^9^c$	1.8×10^9
CO ₂ CH ₃	6.6×10^7	8.5×10^8 $7.1 \times 10^8^c$	2.3×10^9	1.2×10^9
SO ₃ ⁻		6.0×10^8	1.7×10^9	1.3×10^9
CONH ₂	7.3×10^7	4.3×10^8 $4.8 \times 10^8^c$	2.2×10^9	1.2×10^9
CH=NOH		$6.5 \times 10^8^c$	2.0×10^9	1.4×10^9
CO ₂ ⁻		5.9×10^8	$3.1 \times 10^9^f$	$7.4 \times 10^8^f$
H	$< 10^7^g$	$3.3 \times 10^8^g$	$1.6 \times 10^9^g$	
CH ₃		$1.5 \times 10^8^c$	$1.4 \times 10^9^c$	
OCH ₃		$1.1 \times 10^8^c$	$1.2 \times 10^9^c$	1.2×10^8
OH		$7.0 \times 10^7^c$	$1.1 \times 10^9^c$	
NH ₂			$5 \times 10^8^c$	

^a N₂O-saturated aqueous solutions, [alcohol] = 1 M, [nitrobenzene] = 0.2–2 mM, pH 4–5, 20 °C. ^b Measured at λ_{max} of nitroxide (~ 25 nm below λ_{max} of radical anion), accurate to $\pm 20\%$. ^c Measured by conductance detection, accurate to $\pm 10\%$. ^d Measured at λ_{max} of radical anion, accurate to $\pm 10\%$. ^e N₂O-saturated aqueous solutions, [formate] = 0.1 M, [nitrobenzene] = 0.2–1 mM, pH 7, 20 °C, accurate to $\pm 10\%$. ^f Similar value reported by ref 28b. ^g From ref 21.

summarized in Table I. As compared to the corresponding nitroxide radicals, the radical anions are characterized by smaller values for $a(N)$ and larger ones for the ring protons. This shows that, in going from the nitroxide to the radical anion, unpaired spin density is transferred from the nitrogen to the aromatic ring, i.e., the radical anion is a more delocalized radical than the nitroxide.

The production of radical anions via eq 4 was also shown by using the time-resolved optical and conductance detection methods. Concerning the latter, at pH > 7 reaction 4 leads to a decrease in conductance since the highly mobile OH⁻ ion is replaced by the less mobile radical anion. On the basis of equivalent conductances for OH⁻ and the radical anion of 175 and 30 $\Omega^{-1} cm^2$, respectively, the yield of radical anion from reaction 4 was found to be quantitative. The same result was obtained by using optical detection and monitoring the production of radical anion at the λ_{max} values of the absorption bands at 300–360 or 420–560 nm (see Table III).

The rate constants k_{4A} for formation of radical anion 2 by reaction of nitroxide I with OH⁻ were determined in the pH range 7–9. They are in the range 4×10^9 to $10^{10} M^{-1} s^{-1}$, i.e., of a magnitude similar to reactions of OH⁻ with α -hydroxyalkyl radicals.¹⁹ The rate constants k_{4A} were found to be essentially independent of the nature of the substituent R.

In the pH range 9–10 the rates of formation of radical anion become independent of pH but dependent on the concentration of the nitrobenzene (measured up to 2 mM). The (second order) rate constants measured are similar to those determined at pH ≤ 6 for formation of the nitroxide radicals according to eq 1. The dependence on concentration means that at pH 9.5–10 the addition step (eq 1) is rate determining and not step 4A or B. Since this is so for nitrobenzene concentrations up to 2 mM, from the rate constants for eq 1, the rate constant for the (unimolecular) heterolysis of the ionized nitroxide radical, step 4B, can be calculated to be $\geq 5 \times 10^5 s^{-1}$.

At pH ≥ 10 the rate constants for formation of radical anion increase again up to a plateau at pH ≈ 11.5 . This is explained by reaction of the ionized hydroxymethyl radical ($pK = 10.7$) with the nitrobenzenes via eq 5. The rate constants for this electron-

transfer reaction ($k \approx 3 \times 10^9 M^{-1} s^{-1}$)²⁰ are diffusion controlled and essentially independent of the nature of the substituent on the ring.



(2) Reactions of CH₃CHOH. (a) Acid Solutions (pH 3–6). CH₃CHOH was produced by H abstraction from ethanol by the OH (and H) radicals generated by irradiation of (N₂O saturated) aqueous solutions containing 0.1–2 M ethanol. From these reactions the yield of CH₃CHOH is 84%, and the remaining 16% are accounted for by $\dot{C}H_2CH_2OH$, which is not a reducing radical.^{22,23} As with $\dot{C}H_2OH$, the reactions of CH₃CHOH with the nitrobenzenes were studied by using product analysis and in-situ-radiolysis-ESR methods and time-resolved optical and conductance detection techniques. Gas-chromatographic analysis of N₂O-saturated solutions containing, e.g., 1 M ethanol and 2 mM 4-nitrobenzotrile revealed the formation, after ⁶⁰Co- γ -radiolysis, of acetaldehyde. The yield of CH₃CHO was 80–90% of that of OH (i.e., equal to that of CH₃CHOH) and independent of pH in the range 3–10. The same result was obtained with other nitrobenzenes such as 4-nitrobenzoic acid, 4-nitrobenzamide, 4-nitroacetophenone, and nitrobenzene itself.

ESR experiments showed that the reaction of CH₃CHOH with the nitrobenzenes leads to the formation of the corresponding radical anions. Nitroxide radicals of the type formed by $\dot{C}H_2OH$ could not be detected. This information together with that from product analysis could be interpreted to mean that CH₃CHOH reacted with nitrobenzenes by electron transfer. However, from kinetic spectroscopy with optical and conductance detection it became clear that the mechanism is considerably more complicated. The circles and crosses of Figure 2 show the optical absorption spectra observed on reacting CH₃CHOH with 4-nitrobenzotrile (4-NBN) at pH 4 and 10 and 500 μs after initiation of the reaction. At 10 μs the absorption maximum of the species formed is at 310 nm, whereas at 500 μs the spectrum observed

(20) A similar rate constant has been reported by ref 21 for nitrobenzene.

(21) Asmus, K.-D.; Wigger, A.; Henglein, A. *Ber. Bunsenges. Phys. Chem.* **1966**, *70*, 862.

(22) Adams, G. E.; Willson, R. L. *Trans. Faraday Soc.* **1969**, *65*, 2981.

(23) Asmus, K.-D.; Möckel, K.; Henglein, A. *J. Phys. Chem.* **1973**, *77*, 1218.

(19) Laroff, G. P.; Fessenden, R. W. *J. Phys. Chem.* **1973**, *77*, 1283.

Table III. Spectral Parameters of Nitroxide and Anion Radicals of Para-Substituted Nitrobenzenes

substituent	radical anion ^a		nitroxide ^b		conjugate acid of radical anion ^c	
	λ_{\max} , nm	ϵ , M ⁻¹ cm ⁻¹	λ_{\max} , nm	ϵ , M ⁻¹ cm ⁻¹	λ_{\max} , nm	ϵ , M ⁻¹ cm ⁻¹
SO ₃ CH ₃	320	1.76×10^4				
	460	1.5×10^3				
NO ₂	385	1.03×10^4 ^d	335	1.09×10^4	357	1.2×10^4 ^e
	640	4.7×10^3				
CN	330	2.06×10^4 ^f	305	2.09×10^4	305	2.09×10^4 ^g
	480	1.4×10^3 ^f				
SO ₂ NH ₂	320	1.95×10^4				
	450	1.0×10^3				
CHO	360	1.5×10^4 ^f	330	1.45×10^4	330	1.95×10^4 ^g
	565	3.1×10^3 ^f				
CF ₃	300	1.40×10^4				
	430	7.5×10^2				
COCH ₃	350	1.78×10^4	325	1.12×10^4		
	545	2.9×10^3				
CO ₂ CH ₃	335	2.17×10^4 ^f	~320	1.1×10^4	310	2.6×10^4 ^g
	510	1.95×10^3 ^f				
SO ₃ ⁻	320	1.49×10^4				
	440	1.3×10^3				
CONH ₂	330	1.87×10^4				
	480	1.5×10^3				
CO ₂ ⁻	325	1.83×10^4 ^d				
	450	9×10^2				
CH=NOH	350	2.31×10^4				
H	285	1.40×10^4 ^h				
	430	3×10^2 ^h				
OCH ₃	290	1.94×10^4 ^c				
	420	1.0×10^3				
OH	295	2.0×10^4 ⁱ			290	1.24×10^4 ⁱ

^aN₂O-saturated solutions, [formate] = 0.1 M, [nitrobenzene] = 0.1–0.2 mM, pH 7, 20 °C. The ϵ values were calculated by assuming $G(\text{radical anion}) = G(\text{CO}_2^{\cdot-}) = 6.6$. ^bN₂O-saturated solutions, [methanol] = 1–2 M, [nitrobenzene] = 0.5–2 mM, pH 4–5, 20 °C. The ϵ values are based on $G(\text{nitroxide}) = G(\text{CH}_2\text{OH}) = 6.6$. The ϵ values are corrected for depletion of substrate. ^cThe radical was produced by reaction with (CH₃)₂COH. ^dSimilar values are reported by ref 28b. ^eFrom ref 28b. ^fSimilar values are reported by ref 16. ^gFrom ref 16. ^hFrom ref 21. ⁱFrom ref 17.

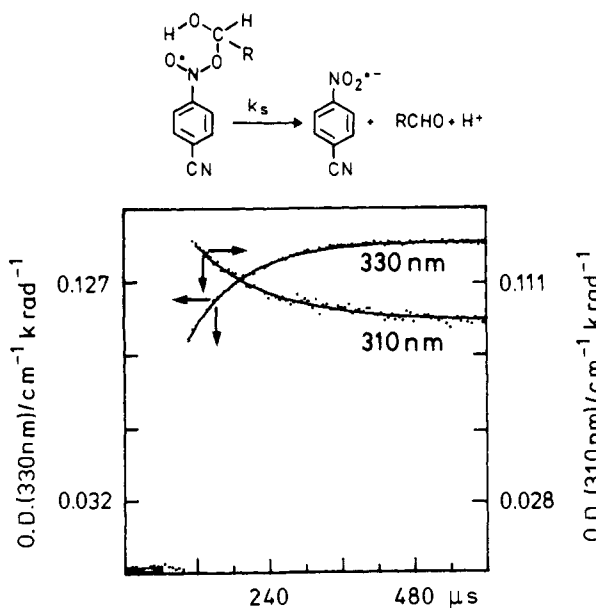


Figure 3. Changes in optical density observed at 310 and 330 nm on production of CH₃CHOH (by a 200-ns electron pulse) in the presence of 1 mM 4-nitrobenzoxime at pH 4–5, 20 °C, [ethanol] = 1 M. The solid line through the experimental points is from a computer fit assuming first-order kinetics.

has a peak at 330 nm and is identical with that of the radical anion as obtained in the reaction of 4-NBN with e_{aq}⁻ or CO₂⁻. Figure 3 shows the kinetics of the changes as observed at 310 and 330 nm: at 310 nm there is a fast increase in optical density (OD) followed by a slow exponential decrease, whereas at 330 nm, after the fast increase, there is a slow further increase of OD which is also exponential in nature and occurs with exactly the same rate as the decrease at 310 nm. The rates of the slow increase/decrease are strictly independent of the concentration of 4-NBN (in the

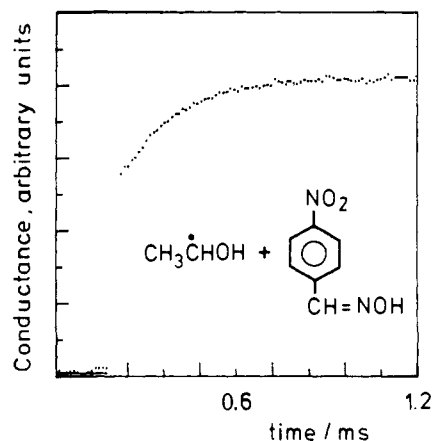


Figure 4. Changes in the conductance of a solution containing 1 M ethanol and 1 mM 4-nitrobenzaldehyde at pH 4–5 and 20 °C induced by production of CH₃CHOH by a 200-ns electron pulse. The slow increase, after the step, is due to decomposition of the nitroxide (see text).

range 0.1–4 mM) and of pH (in the range 3–6.5), but they are dependent on temperature. The rate of the *fast* increase in OD, as measured at 310 nm, is linearly dependent on the concentration of 4-NBN up to 1 mM, and from this dependence the rate constant for reaction of CH₃CHOH with 4-NBN was determined to be 1.2×10^9 M⁻¹ s⁻¹.

The existence of two components in the formation of radical anion can also be seen by using conductance detection. As an example, Figure 4 shows that in the reaction of CH₃CHOH with 4-nitrobenzaldehyde at pH 4 there is a fast buildup of conductance followed by a slow further increase which is exponential in nature. The slow increase is independent of the concentration of the nitro compound (in the range 0.1–4 mM) and pH (pH 3–6). At the same temperature, the rate of the slow component of the conductance increase is identical with that measured optically for the unimolecular formation of radical anion, and after completion

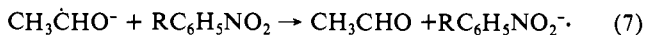
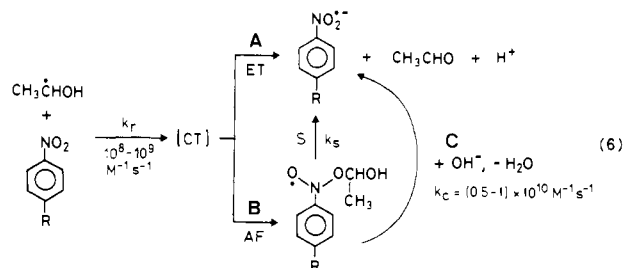
of the reaction the yield of H^+ is equal with that of $CH_3\dot{C}HOH$.

In contrast to the slow component, the rate of conductance increase from the fast component was found to increase linearly with the concentration of the nitro compound in the range 0.2–1 mM. The rate constants $k_{R(ET)}$ (eq 6A) determined from this dependence (Table II) vary from 7×10^7 for 4-nitrophenol to $2.3 \times 10^9 M^{-1} s^{-1}$ for 1,4-dinitrobenzene. Within experimental accuracy ($\pm 10\%$) the rate constants are equal with those measured optically for the fast formation of radical anion. The same rate constants were also found by monitoring the absorption at wavelengths ~ 25 nm below λ_{max} (radical anion). At these lower wavelengths the nitroxide radicals have higher ϵ than the radical anions (see Figures 2 and 3). However, the spectra of the nitroxide and anion radicals still overlap strongly which makes it impossible to measure with high precision the separate rate constants $k_{R(AF)}$ for formation of nitroxide.

(b) **Alkaline Solutions.** In contrast to the pH range 3–6, in which the rate of the concentration-independent and "slow" formation of H^+ or radical anion is independent of pH, at pH 7–10 the rates of the "slow" radical anion formation increase with pH according to the equation $k_{obsd} = k_s + k_c[OH^-]$. The k_c values are in the range $(0.5-1) \times 10^{10} M^{-1} s^{-1}$ and essentially independent of the nature of the substituent R at the benzene ring. The situation is similar to that with $\dot{C}H_2OH$.

At pH $\geq 10-10.5$ the step in the formation of radical anion disappears and the rates become dependent on the concentration of the nitro compound. The explanation has to do with the ionization of $CH_3\dot{C}HOH$ ($pK_a = 11.3$). $CH_3\dot{C}HO^-$ reacts with the nitrobenzenes by electron transfer (eq 7). The rate constants for this reaction are independent of the nature of R and of the order $\sim 4 \times 10^9 M^{-1} s^{-1}$, i.e., slightly larger than those for $\dot{C}H_2O^-$.

(c) **Reaction Scheme.** The results so far described are explained by reaction scheme in eq 6 and 7. The reaction of $CH_3\dot{C}HOH$



yields two products: the radical anion (step 6A) and a nitroxide type radical analogous to that observed in the case of reaction of $\dot{C}H_2OH$ (step 6B). The rate constants for the two processes 6A (determined by optical and by conductance detection) and 6B (determined optically) are equal within the experimental error of 10% (see Table II).

The fact that in the reaction between $CH_3\dot{C}HOH$ and the nitrobenzenes two different products are formed with apparently equal rate constants but in yield ratios that differ significantly from 1:1 (Table IV, third column) is interpreted in terms of a common intermediate for the radical anion and the adduct. The intermediate, which may be conceived of as a charge transfer or π complex, decays via paths 6A and B to the observed radicals. From the linearity of the dependence of the rate constants for formation of radical anion or adduct on nitrobenzene concentrations up to 2 mM and the experimentally observed rate constant k_R ($10^9 M^{-1} s^{-1}$), the rate constants for decomposition of the complex are calculated to be $\geq 2 \times 10^6 s^{-1}$ (for the case of 4-NBN).

The nitroxide undergoes a spontaneous fragmentation to give the radical anion, CH_3CHO , and H^+ (step 6S, first-order rate constant k_s). The rate of formation of radical anion from the adduct is increased in the presence of OH^- (reaction 6C). The rate constants for this catalyzed decomposition of the nitroxide are $(0.5-1) \times 10^{10} M^{-1} s^{-1}$.

As with $\dot{C}H_2O^-$, the reaction of the ethanol radical anion with the nitrobenzenes (eq 7) appears to proceed by electron transfer.

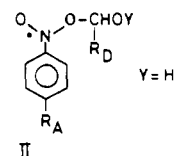
Table IV. Reaction of $CH_3\dot{C}HOH$ with Para-Substituted Nitrobenzenes; Dependence on the Substituent R of f_{ET} , the Fraction of Electron Transfer, and of k_s , the Rate Constant for Spontaneous Heterolysis of the Nitroxide^a

R	Hammett		k_s, s^{-1}	notes
	σ_p^b	f_{ET}^c		
SO ₂ CH ₃	0.90	0.81	$1.2 \times 10^4 c,d$	$k_s(H_2O)/k_s(D_2O) = 2.2$
NO ₂	0.81	0.94	$5.3 \times 10^4 d$	
CN	0.70	0.77	$1.0 \times 10^4 c,d$	
SO ₂ NH ₂	0.58	0.80	$8.1 \times 10^3 c,d$	$k_s(H_2O)/k_s(D_2O) = 2.2$
CF ₃	0.53	0.70	$6.8 \times 10^3 c,d$	
COCH ₃	0.47	0.84	$1.5 \times 10^4 c,d$	
CO ₂ H	0.44	0.86 ^d	$1.3 \times 10^4 d$	
CO ₂ CH ₃	0.44	0.81	$8.1 \times 10^3 c,d$	
SO ₃ ⁻	0.37	0.64 ^d	$4.7 \times 10^3 d$	
CONH ₂	0.31	0.75	$6.3 \times 10^3 c,d$	
Br	0.26	0.49	$2.3 \times 10^3 c$	
Cl	0.24	0.50	$1.8 \times 10^3 c$	
I	0.21	e	$2.8 \times 10^3 c$	
CO ₂ ⁻	0.11	0.61 ^d	$3.6 \times 10^3 d$	
CH=NOH	0.1	0.60	$4.0 \times 10^3 c,d$	
F	0.06	0.69	$1.9 \times 10^3 c$	
CH ₂ OH	0.01	0.37	$1.5 \times 10^3 c,d$	
H	0.00	0.50	$1.2 \times 10^3 c,d$	
CH ₃	-0.14	0.28	$7 \times 10^2 c$	
OCH ₃	-0.28	0.35	$8 \times 10^2 c$	
OH	-0.38	0.40	$4 \times 10^2 c$	
NH ₂	-0.57	<0.05	< $10^2 c$	

^a N₂O-saturated aqueous solutions, pH 4–5. [Ethanol] = 0.1–1 M, [nitrobenzene] = 0.5–2 mM, 20 °C. ^b From ref 32. ^c From conductance measurements. ^d Determined by using optical detection. Where optical and conductance measurements were performed, the rate constants given are the average from both methods (error limits $\pm 10\%$). ^e Not determinable due to insufficient solubility.

There was no evidence for an intermediate or a delayed formation of radical anion up to nitrobenzene concentrations of 4 mM; i.e., the lifetime of a hypothetical adduct must be < 50 ns.

(d) **Mechanistic Studies on the Spontaneous Heterolysis of the Adduct (Reaction 6S).** In order to obtain a detailed picture of the factors that influence reaction 6S, a systematic study of the effects of structure of the adduct II, of solvent, and of temperature was performed. Concerning structure it is particularly relevant to change (a) the electron deficiency of the electron-acceptor part of the molecule (the nitrobenzene) and (b) the electron-donating power of the donor part (the alcohol). The electron-accepting power was varied by changing the substituent R_A at the benzene ring, and the electron-donating power via R_D on the alcohol part:



The results are contained in Tables IV–VI and in Figures 5–7.

As seen from Table IV, the rate constant k_s and the fraction of electron transfer, $f_{et} \equiv k_{6A}/(k_{6A} + k_{6B})$, depend on the substituent R_A at the benzene ring: k_s and f_{ET} increase with increasing electron-withdrawing power of R_A. For both k_s and f_{ET} a Hammett relation is obeyed. For k_s a Hammett ρ of 1.4 ± 0.1 is obtained. An analogous correlation is obtained by plotting $\log k_s$ vs. the pK_a values of the corresponding radical anions (Brønsted plot). In this case the slope $\alpha = -(1.4 \pm 0.1)$. It is interesting that there is also a correlation between k_s and $a(N)$, the ESR coupling constants of the nitrogen atoms of the anion or nitroxide radicals: k_s decreases with increasing $a(N)$. A similar correlation has been found²⁹ between $a(N)$ of the radical anion and the rate constants for reaction of $(CH_3)_2\dot{C}OH$ with the parent nitrobenzenes.

In Table V are listed the activation parameters for the heterolysis of II as a function of R_A. The ΔH^\ddagger values are relatively small (5–10 kcal mol⁻¹). The ΔS^\ddagger values are strongly negative.

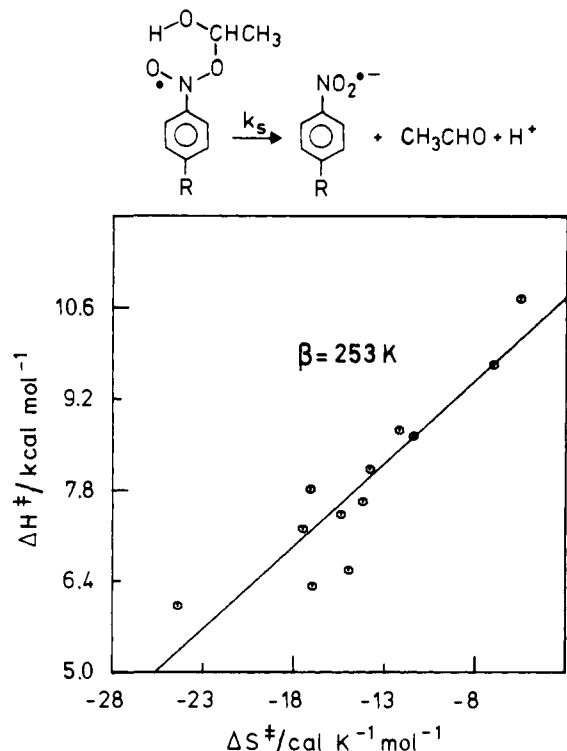


Figure 5. Isokinetic Hammett plot for the heterolysis of *p*-CH₃CH(OH)ON(O)C₆H₄R—the dependence of ΔH^\ddagger on ΔS^\ddagger for a series of different R's. The slope of the straight line through the data points (from Table V) corresponds to an isokinetic temperature of 253 K.

Table V. Effect of Substituent R_A on the Activation Parameters for the Heterolysis of *p*-CH₃CH(OH)ON(O)C₆H₄R_A^a

R _A	ΔH^\ddagger , kcal mol ⁻¹	ΔS^\ddagger , cal K ⁻¹ mol ⁻¹
SO ₃ CH ₃	9.7	-7
NO ₂	6.6	-15
CN	7.6	-14
SO ₂ NH ₂	7.4	-15
CF ₃	10.7	-6
COCH ₃	6.3	-17
CO ₂ CH ₃	8.6	-11
SO ₃ ⁻	8.7	-12
CONH ₂	8.1	-14
Cl	7.2	-19
CH=NOH	7.2	-18
H	7.2	-17
CH ₃	7.8	-16
OCH ₃	5.4	-24

^a N₂O-saturated aqueous solutions, pH 4–5, [ethanol] = 1–2 M, [*p*-O₂NC₆H₄R] = 0.5–2 mM. ^b ΔS^\ddagger and ΔH^\ddagger refer to 293 K.

Concerning the influence of the substituent R_A, there is no simple relation between the $\sigma(R_A)$ and the ΔH^\ddagger or ΔS^\ddagger values. The variation in the ΔS^\ddagger values is larger than that of the ΔH^\ddagger values. Figure 5 represents an "isokinetic Hammett plot", i.e., a plot of the ΔH^\ddagger vs. the ΔS^\ddagger values, for the compounds listed in Table V, which differ only with respect to the nature of R_A. A straight line is obtained, the slope of which corresponds to an isokinetic temperature β of 253 K, which is less than the experimental temperature range (268–313 K). According to isokinetic theory²⁴ this means that with respect to the effect exerted by the substituent on the benzene ring, the heterolysis of the nitroxide II is entropy controlled. An analogous result is obtained with the effects of a variation of the electron-donating power of R_D, the electron-donating part of II. Table VI contains the rate constants and activation parameters for decomposition of II with R_A = CN and different R_D's. The rate constants increase with increasing

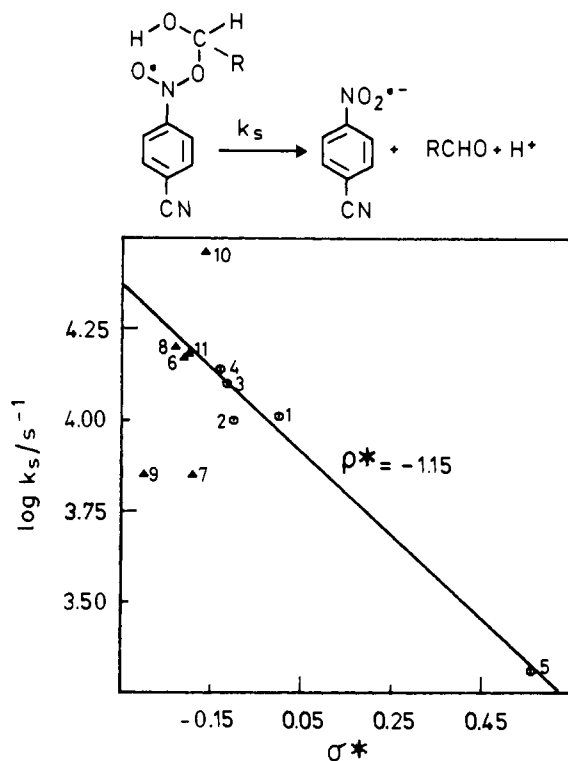


Figure 6. Taft plot for the heterolysis of *p*-RCH(OH)ON(O)C₆H₄CN. The numbers identify R by reference to the entries in Table VI. The straight line is a least mean square fit through points 1–5 (nonbranched R's). The slope corresponds to $\rho^* = -1.15$.

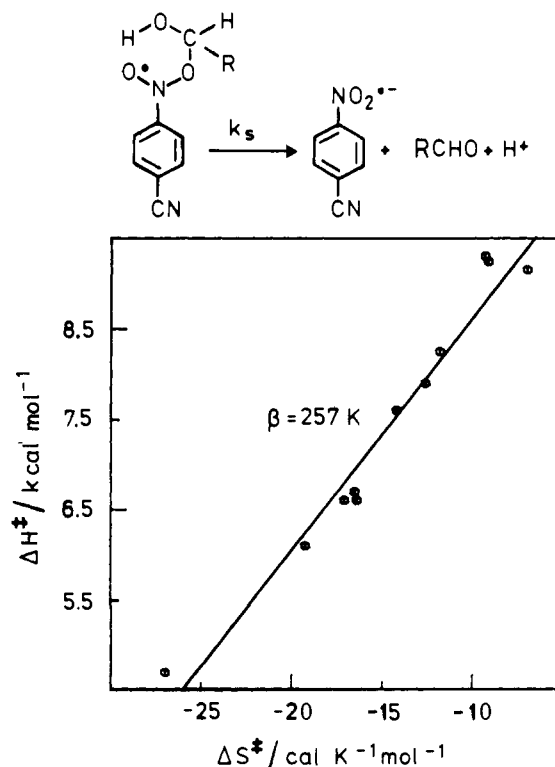


Figure 7. Isokinetic Taft plot for the heterolysis of *p*-RCH(OH)ON(O)C₆H₄CN—the dependence of ΔH^\ddagger on ΔS^\ddagger for a series of different R's. The slope of the straight line through the data points (from Table VI) gives an isokinetic temperature of 257 K.

electron-donating strength of R_D. For the nonbranched R_D's and only for these, a Taft relation is well obeyed, as shown in Figure 6. ρ^* is equal to -1.15. Figure 7 ("isokinetic Taft plot") shows that the variation of R_D results in a linear dependence of ΔH^\ddagger on ΔS^\ddagger . The isokinetic temperature β is equal to 257 K, i.e., below

(24) See, e.g.: (a) Leffler, J. E.; Grunwald, E. "Rates and Equilibria of Organic Reactions"; J. Wiley: New York, 1963. (b) Exner, O. *Collect. Czech. Chem. Commun.* 1972, 37, 1425.

Table VI. Effect of Substituent R_D on the Rate Constants^a and Activation Parameters for the Heterolysis of p - R_D CH(OH)ON(O) C_6H_4CN

no.	R_D	σ^*	k_s, s^{-1}	$\Delta H^\ddagger, kcal\ mol^{-1}$	$\Delta S^\ddagger, cal\ K^{-1}\ mol^{-1}$	notes
1	CH ₃	0.0	1.0×10^4	7.6	-14	$k_s(H_2O)/k_s(D_2O) = 2.2$
2	CH ₃ CH ₂	-0.10	1.0×10^4	6.1	-19	
3	CH ₃ CH ₂ CH ₂	-0.115	1.3×10^4	7.9	-13	
4	CH ₃ CH ₂ CH ₂ CH ₂	-0.13	1.4×10^4	8.3	-12	
5	HOCH ₂	0.56	2.0×10^3	4.7	-27	$k_s(H_2O)/k_s(D_2O) = 1.5$
6	CH ₃ CH ₂ C(CH ₃)H	-0.21	1.5×10^4	6.6	-16	
7	(CH ₃) ₂ CH	-0.19	7.1×10^3	9.2	-9	
8	(C ₂ H ₅) ₂ CH	-0.23	1.6×10^4	6.7	-17	
9	C(CH ₃) ₃	-0.30	7.0×10^3	9.3	-9	
10	C(CH ₃) ₃ CH ₂	-0.165	2.9×10^4	9.2	-7	
11	cyclopentyl	-0.20	1.5×10^4	6.6	-17	

^a N₂O-saturated aqueous solutions. [Alcohol] = 0.1–1 M, [4-nitrobenzonitrile] = 1 mM, pH 4–5, 20 °C.

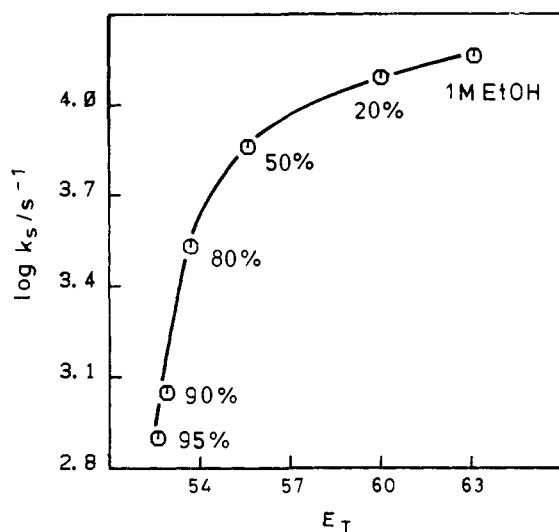


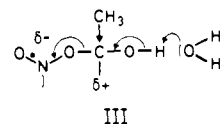
Figure 8. Heterolysis of p -CH₃CH(OH)ON(O) C_6H_4CN in N₂O-saturated ethanol/water mixtures—the dependence of $\log k_s$ on solvent polarity as measured by E_T ; [4-nitrobenzonitrile] = 2 mM, 30 °C. The E_T values are from ref 27.

the experimental range. From this value it is clear that the heterolysis reaction is entropy controlled with respect to the effect of R_D . In other words, as with R_A , the effect of the substituent on reaction rate is exerted predominantly by its influence on the activation entropy. This also qualitatively explains why the k_s values for the branched R_D 's deviate from the straight line in the Taft plot (Figure 6). Obviously the branched R_D 's exert on ΔH^\ddagger and ΔS^\ddagger an influence different from that of the nonbranched R_D 's.

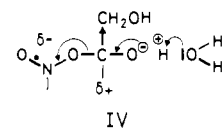
Of particular importance are the negative sign and the magnitude of the ΔS^\ddagger values. Values of -12 to -20 eu indicate extensive reorganization of the solvent shell in the transition state as a result of hydration of (incipient) ions, specifically, the proton. The entropy change on hydration of a proton by four water molecules to yield the hydronium ion $H(H_2O)_4^+$ is -24 eu.²⁵ The fact that the experimental values are more positive than this value is suggested to be due to the positive contribution that results from the increase in number of molecules in going from the adduct to the radical anion, the oxo compound, and H^+ . That it is the hydration of the proton that leads to the negative ΔS^\ddagger values can be unequivocally shown by replacing it by alkyl (i.e., in II, Y = alkyl). In this case, the positive ion formed in the transition state is a carbocation, which becomes much less hydrated than the proton. For these systems, the experimentally observed ΔS^\ddagger values are positive (~15 eu).²⁶ The same situation exists with the heterolysis of the nitroxide formed by addition of α -alkoxyalkyl radicals to tetranitromethane; the ΔS^\ddagger values are again positive,⁹ since the positive ion formed in the transition state is a carbocation and not a proton.

If deprotonation occurs in the transition state as concluded from the negative ΔS^\ddagger values, there should be a kinetic isotope effect for k_s in going from H₂O to D₂O. This was checked by using two nitrobenzenes (4-NBN and 4-nitro(trifluoromethyl)benzene) and two alcohol radicals (CH₃CHOH and HOCH₂CHOH). With CH₃CHOH, $k_s(H_2O)/k_s(D_2O)$ at 20 °C was found to be 2.2 ± 0.1 for both nitrobenzenes. However, with HOCH₂CHOH the ratio is only 1.5 ± 0.1 , again independent of the nitrobenzene. This difference between CH₃CHOH and HOCH₂CHOH can be understood in terms of the different stabilities of the (incipient) cations III and IV. Due to the -I effect of the OH group in the β position, IV is expected to be less stable than III. Besides resulting in a reduction of k_s (Table VI), this leads to an increased tendency to deprotonate at an early stage of the transition state, i.e., deprotonation tends to precede the heterolysis of the C–O bond.

This is symbolized below:



III
synchronous O–H
and C–O bond breaking



IV
O–H deprotonation (partly)
preceding C–O bond breaking

A reaction between neutral molecules that proceeds via a polar transition state should be sensitive to variation of the solvent polarity. This was tested by performing the reaction in ethanol–water mixtures. A two-step way of production of radicals i.e., via a fast (bimolecular) and a slow (unimolecular) process, was noticeable in mixtures with up to 95% (v/v) ethanol. The relative step height of the fast component decreased from 77% for 1 M ethanol in water to 47% in an ethanol/water 95:5 mixture. The rates of both processes decreased systematically with increasing ethanol content.

Figure 8 shows the dependence of k_s on the polarity of the medium, expressed²⁷ in terms of E_T values. From the plot it is clear that the k_s value extrapolated to pure ethanol is $\ll 10^2\ s^{-1}$ and that the effect on k_s of adding H₂O to ethanol is drastic in the range of small total water concentrations but levels off at high water content. This type of dependence is in support of the mechanism presented. A similar dependence on solvent polarity was found⁹ for the heterolysis of nitroxide radicals from α -alkoxyalkyl radicals and tetranitromethane.

(3) Reactions of (CH₃)₂COH. (CH₃)₂COH was generated by H abstraction from propan-2-ol by the OH and H radicals pro-

(25) See: Buschmann, H.-J.; Dutkiewicz, E.; Knoche, W. *Ber. Bunsenges. Phys. Chem.* **1982**, *86*, 129.

(26) Steenken, S., unpublished material.

(27) Reichardt, C. in "Molecular Interactions", Ratajczak, H., Orville-Thomas, W. J., Eds.; J. Wiley: New York, 1982; Vol. 3, p 241.

duced by irradiation of aqueous solutions containing 0.1–2 M propan-2-ol. The yield of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ from these reactions is 86%, and the remaining 14% are due to $\dot{\text{C}}\text{H}_2(\text{CH}_3)\text{CHOH}$, which has no reducing properties.^{22,23} The reactions of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ with the nitrobenzenes were studied by using the same techniques as described in the cases of $\dot{\text{C}}\text{H}_2\text{OH}$ and $\text{CH}_3\dot{\text{C}}\text{HOH}$. As revealed by gas-chromatographic analysis of ^{60}Co - γ -irradiated aqueous solutions containing, e.g., 1 M propan-2-ol and 2 mM 4-nitrobenzonitrile or 4-nitrobenzoic acid, the reaction of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ with these nitro compounds leads to the production of acetone. The yield of acetone was found to be 80–90% of that of OH (i.e., equal to that of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$) and independent of pH in the range 3–10. This shows that $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ is quantitatively oxidized by one-electron transfer.

The results of ESR experiments are in support of this picture, since only radical anions were seen on reaction of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ with nitrobenzenes such as, e.g., 4-nitrobenzonitrile, 4-nitrobenzoic acid, and nitrobenzene itself, in agreement with earlier studies.^{13,28b,29} Nitroxide radicals of the type formed in the case of $\dot{\text{C}}\text{H}_2\text{OH}$ could not be detected. In order to further test for the potential formation of (short-lived) nitroxide radicals, time-resolved experiments with optical and conductance detection were performed. With all nitrobenzenes from 1,4-dinitrobenzene to 4-nitrotoluene an undelayed formation of the radical anions was observed up to 1 mM nitro compound, in agreement with earlier studies.^{21,22,28b,29} The rate constants for formation of radical anion and H^+ by reaction of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ with these compounds (Table II) as obtained from the linear dependencies of the rates of formation on the concentrations of the nitrobenzenes (0.2–1 mM) are between 2×10^9 and $3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and rather insensitive to the substituent R from R = H to NO_2 , but they decrease below the diffusion level if R is electron donating. In order for these dependencies to be linear up to 1 mM, the lifetimes of potential nitroxide intermediates must be $\leq 1/10^{-3}(2 \times 10^9) \text{ s}^{-1} = 0.5 \mu\text{s}$.

As determined by optical and conductometric detection, the yields of radical anion were 80–90% of that of OH + H, i.e., equal to that of acetone and of its precursor, $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$.

A search was made for nitroxide formation in the reaction of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ with nitrobenzenes containing the strongly electron-donating groups CH_3O , HO , H_2N , and $(\text{CH}_3)_2\text{N}$. As already mentioned, with 4-nitrotoluene, no delayed formation of radical anion was seen up to nitrobenzene concentrations of 2 mM. Since the reaction rate constant is $1.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, this observation means that the lifetimes of potential intermediates must be $\leq 0.3 \mu\text{s}$. However, with 4-nitroanisole ($\sigma(\text{CH}_3\text{O}) = -0.28$) the increase of k_{obsd} with increasing [4-nitroanisole] leveled off starting at 1–2 mM to give a maximum value of $k_{\text{obsd}} \approx (1-2) \times 10^6 \text{ s}^{-1}$. With 4-nitrophenol ($\sigma(\text{OH}) = -0.38$) a plateau value corresponding to $k_{\text{obsd}} \approx 5 \times 10^5 \text{ s}^{-1}$ was found. These values are suggested to represent k_s , the rate constant for the spontaneous heterolysis of the $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ adduct to 4-nitroanisole or to 4-nitrophenol. With 4-nitroaniline ($\sigma(\text{NH}_2) = -0.57$), the formation of radical anion, as measured by the conductance technique at pH 4–5, occurred in two steps: After a fast one, which accounted for 36% of the total conductance change, there was a slow further increase of conductance. The rate of fast conductance production increased with increasing 4-nitroaniline concentration (0.2–1 mM), whereas the rate of the slow process was found to be independent of the 4-nitroaniline concentration in the range 0.1–2 mM. At 20 °C, the rate constant for the unimolecular process that leads to the production of H^+ is $k_s = 2.1 \times 10^3 \text{ s}^{-1}$. This behavior shows that $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ reacts with 4-nitroaniline like the weaker reductant² $\text{CH}_3\dot{\text{C}}\text{HOH}$ does with the nitrobenzenes (Table IV) that are stronger oxidants than 4-nitroaniline.

With 4-nitro-*N,N*-dimethylaniline ($\sigma(\text{N}(\text{CH}_3)_2) = -0.83$), no conductance change was observed at pH 4.6–6 up to 4 ms after initiation of the reaction with $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$. However, at pH > 7 an OH^- -catalyzed production of H^+ was seen. These results are

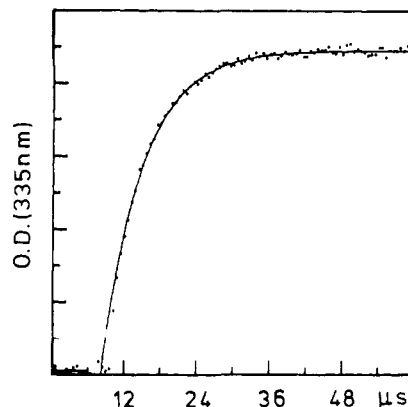
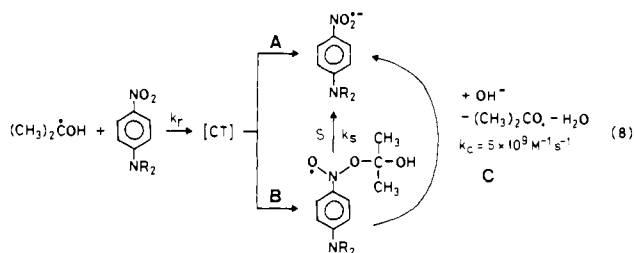


Figure 9. Formation of the 4-nitrobenzonitrile radical in N_2O -saturated Pr-2-OH/water mixtures 95:5, observed at 335 nm: 20 °C, [4-nitrobenzonitrile] = 2 mM. The line through the points is from a computer fit assuming first-order kinetics.

explained in terms of nitroxide formation by reaction of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ with the nitro compound analogous to eq 1 and 4. From the dependence of the rate of loss of OH^- as a function of $[\text{OH}^-]$, the rate constant for reaction of OH^- with the nitroxide-type adduct of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ to 4-nitro-*N,N*-dimethylaniline was found to be $5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$, a value similar to those for reaction of OH^- with the adducts of $\dot{\text{C}}\text{H}_2\text{OH}$ and $\text{CH}_3\dot{\text{C}}\text{HOH}$ with the nitrobenzenes as discussed in sections 1 and 2. Since a spontaneous decomposition of the nitroxide was not seen within 4 ms, the rate constant for such a process must be $< 2 \times 10^2 \text{ s}^{-1}$. The reactions of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ with the nitroanilines are summarized in scheme 8. For R = H, A:B \approx 1:2 and $k_s = 2.1 \times$



s^{-1} . For R = CH_3 , A:B \leq 1:9 and $k_s \leq 2 \times 10^2 \text{ s}^{-1}$. It is interesting to note that with respect to 4-nitro-*N,N*-dimethylaniline $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ behaves like the much weaker reductant³ $\dot{\text{C}}\text{H}_2\text{OH}$ does with respect to all the nitrobenzenes studied (section 1).

For the nitrobenzenes with substituents having $\sigma_p > \sigma_p(\text{OCH}_3)$, the formation of radical anion could proceed via eq 8A or 8B or both eq 8A and 8B. If path B was involved, k_s would have to be $> 2 \times 10^6 \text{ s}^{-1}$. In order to get further information on adduct formation between $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ and nitrobenzenes containing an electron-withdrawing substituent, the reaction of $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ with 4-nitrobenzonitrile was studied in mixtures of propan-2-ol and water with use of optical kinetic spectroscopy. On pulse irradiation of N_2O -saturated propan-2-ol/water 95/5 (v/v) containing 0.2–4 mM 4-nitrobenzonitrile, a radical was produced with a spectrum very similar to that (Figure 2) of the radical anion in water. On this basis the radical in propanol/water 95:5 is assigned to the nitro radical anion or its conjugate acid. The rate of formation of the nitro radical was found to be independent of the concentration of 4-nitrobenzonitrile in the range 1–4 mM. At 20 °C, the rate constant measured was $1.5 \times 10^4 \text{ s}^{-1}$ and there was *no fast* step visible (see Figure 9). This is interpreted in terms of formation of the nitro radical via exclusive ($\geq 90\%$) addition followed by unimolecular decomposition of the adduct, i.e., by eq 8B/S and analogous to eq 6B/S. This demonstrates that what appears to be pure electron transfer in water can be changed into pure addition by simply changing the solvent polarity. As described in section 2, the behavior of $\text{CH}_3\dot{\text{C}}\text{HOH}$ under similar conditions is different since it reacts via a fast *and* a delayed path even in 95% ethanol. The reason for this difference between

(28) (a) Meisel, D.; Neta, P. *J. Am. Chem. Soc.* **1975**, *97*, 5198. (b) Neta, P.; Simic, M. G.; Hoffman, M. Z. *J. Phys. Chem.* **1976**, *80*, 2018.
(29) Neta, P.; Meisel, D. *J. Phys. Chem.* **1976**, *80*, 519.

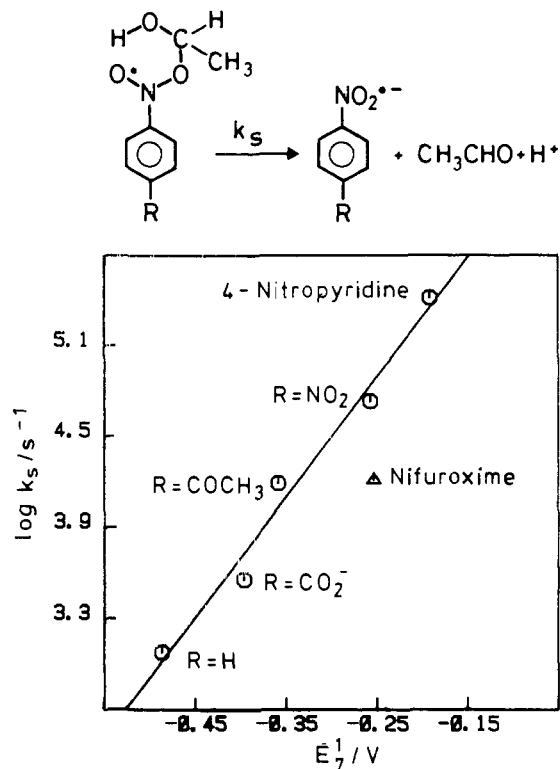


Figure 10. Marcus plot for the heterolysis of p - $\text{CH}_3\text{CH}(\text{OH})\text{ON}(\text{O})\text{C}_6\text{H}_4\text{R}$. The redox potentials are from ref 28. The slope of the line corresponds to 1/127 mV. The point for *anti*-5-nitro-2-furaldoxime (nifuroxime) is included for comparison.

$\text{CH}_3\dot{\text{C}}\text{HOH}$ and $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ is at present unknown.

Summary and Conclusions

Summary. Reaction of $\text{CH}_3\dot{\text{C}}\text{HOH}$ with substituted nitrobenzenes yields the radical anion of the nitrobenzene via a direct and a delayed path (Figures 2-4). The delayed formation is due to unimolecular decomposition (heterolysis) of a nitroxide-type radical produced by covalent bond formation between radical and the nitro group (reaction scheme 6).

The rate constants k_s for decomposition of the adducts depend on the substituent R at the benzene and at the alcohol in a way expected by a push-pull mechanism with R_D pushing and R_A pulling electron density (see structure II). The isokinetic plots (Figures 5 and 7) show that the heterolysis reaction is entropy controlled. $k_{\text{H}_2\text{O}}/k_{\text{D}_2\text{O}} = 2.2$ and ΔS^\ddagger having negative values indicate that deprotonation occurs in the transition state (together with C-O bond heterolysis).

The effect of substitution at C_α in $\dot{\text{C}}_\alpha\text{OH}$ is very drastic: $\dot{\text{C}}\text{H}_2\text{OH}$ reacts only by adduct formation and k_s 's are $< 10^2 \text{ s}^{-1}$, whereas with $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ the k_s values are $> 10^6 \text{ s}^{-1}$ or, alternatively, $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$ reacts by direct electron transfer. However, part of the effect of substitution at C_α can be compensated by varying the substituent R_A at the benzene: With $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, in order to make $k_s < 10^6 \text{ s}^{-1}$, R_A has to be strongly electron donating (example, 4-nitroaniline); with $\dot{\text{C}}\text{H}_2\text{OH}$, in order to make $k_s > 10^2 \text{ s}^{-1}$, R_A has to be strongly electron withdrawing. An example for this is the reaction between $\dot{\text{C}}\text{H}_2\text{OH}$ and 4-nitro-

benzenediazonium tetrafluoroborate ($\sigma_p(\text{N}_2^+) = 1.91$). On the basis of conductance experiments for this system, the rate constant for heterolysis of the hypothetical nitroxide is estimated to be $\geq 10^4 \text{ s}^{-1}$. Another example, although it involves not the benzene but the pyridine system, is the reaction between $\dot{\text{C}}\text{H}_2\text{OH}$ or $\text{CH}_3\dot{\text{C}}\text{HOH}$ with 4-nitropyridine. Due to the electron-withdrawing effect of the nitrogen in the ring, 4-nitropyridine is much more electron deficient than nitrobenzene and even nitrobenzenes carrying electron-withdrawing substituents such as NO_2 . This is reflected by the one-electron redox potentials²⁸ of the nitro compounds. With $\dot{\text{C}}\text{H}_2\text{OH}$, 4-nitropyridine forms an adduct ($k_R = 1.0 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) which at 20 °C undergoes heterolysis with $k_s = 3.2 \times 10^3 \text{ s}^{-1}$ (determined conductometrically) to be compared with $< 10^2 \text{ s}^{-1}$ for the case of nitrobenzenes. With $\text{CH}_3\dot{\text{C}}\text{HOH}$ the corresponding heterolysis reaction has $k_s = 2.6 \times 10^5 \text{ s}^{-1}$ at 20 °C, to be compared with $1.2 \times 10^3 \text{ s}^{-1}$ for nitrobenzene (Table IV). In fact, the dependence of the rate constants k_s on the redox potential of the nitrobenzene follows a Marcus relationship³⁰ (Figure 10, slope = 1/127 mV). Since the heterolysis reaction involves the transfer of electron pairs and not of a single electron, this is another example for the applicability³¹ of the Marcus relation to group-transfer processes.

As a conclusion, it has been shown that the one-electron reduction of nitrobenzenes by α -hydroxyalkyl radicals proceeds predominantly by addition/elimination and that the rates of addition and of elimination are strongly influenced by the electron-donating or -withdrawing properties of the reactants or the components of the adduct. Electron transfer via addition/elimination constitutes a case of organic inner-sphere electron transfer. As compared to direct (outer sphere) electron transfer, addition/elimination provides a path for circumvention of the extreme solvent reorganization necessary in the transition state of the former mechanism.

Registry No. NO_2 - p - $\text{C}_6\text{H}_4\text{SO}_3\text{Me}$, 6214-20-6; NO_2 - p - $\text{C}_6\text{H}_4\text{NO}_2$, 100-25-4; NC - p - $\text{C}_6\text{H}_4\text{NO}_2$, 619-72-7; NH_2SO_2 - p - $\text{C}_6\text{H}_4\text{NO}_2$, 6325-93-5; CHO - p - $\text{C}_6\text{H}_4\text{NO}_2$, 555-16-8; CF_3 - p - $\text{C}_6\text{H}_4\text{NO}_2$, 402-54-0; $\text{CH}_3\text{C}(\text{O})$ - p - $\text{C}_6\text{H}_4\text{NO}_2$, 100-19-6; $\text{MeOC}(\text{O})$ - p - $\text{C}_6\text{H}_4\text{NO}_2$, 619-50-1; NO_2 - p - $\text{C}_6\text{H}_4\text{SO}_3^-$, 30904-42-8; $\text{NH}_2\text{C}(\text{O})$ - p - $\text{C}_6\text{H}_4\text{NO}_2$, 619-80-7; $\text{HON}=\text{CH}$ - p - $\text{C}_6\text{H}_4\text{NO}_2$, 1129-37-9; NO_2 - p - $\text{C}_6\text{H}_4\text{CO}_2^-$, 2906-29-8; PhNO_2 , 98-95-3; Me - p - $\text{C}_6\text{H}_4\text{NO}_2$, 99-99-0; MeO - p - $\text{C}_6\text{H}_4\text{NO}_2$, 100-17-4; HO - p - $\text{C}_6\text{H}_4\text{NO}_2$, 100-02-7; NH_2 - p - $\text{C}_6\text{H}_4\text{NO}_2$, 100-01-6; $\dot{\text{C}}\text{H}_2\text{OH}$, 2597-43-5; $\text{CH}_3\dot{\text{C}}\text{HOH}$, 2348-46-1; $(\text{CH}_3)_2\dot{\text{C}}\text{OH}$, 5131-95-3; CO_2^- , 85540-96-1; MeOSO_2 - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 91948-72-0; NO_2 - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34505-33-4; NC - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 12402-47-0; NH_2SO_2 - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 91948-73-1; CHO - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34512-33-9; CF_3 - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 35848-46-5; $\text{CH}_3\text{C}(\text{O})$ - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34512-32-8; HO_2C - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34473-11-5; $\text{MeOC}(\text{O})$ - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34480-12-1; SO_3 - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 91948-74-2; $\text{NH}_2\text{C}(\text{O})$ - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 69979-66-4; Cl - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34473-09-1; $^-\text{O}_2\text{C}$ - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34537-99-0; $\text{HON}=\text{CH}$ - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 64162-02-3; F - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34467-53-3; HOCH_2 - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 51546-73-7; PhNO_2^- , 12169-65-2; Me - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34509-96-1; MeO - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34473-10-4; HO - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34536-22-6; NH_2 - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34507-63-6; ^-O - p - $\text{C}_6\text{H}_4\text{NO}_2^-$, 34527-30-5; MeOSO_2 - p - $\text{C}_6\text{H}_4\text{N}(\text{O})\text{CH}_2\text{OH}$, 91948-75-3; NC - p - $\text{C}_6\text{H}_4\text{N}(\text{O})\text{CH}_2\text{OH}$, 91948-76-4; HO_2C - p - $\text{C}_6\text{H}_4\text{N}(\text{O})\text{CH}_2\text{OH}$, 91948-77-5; SO_3 - p - $\text{C}_6\text{H}_4\text{N}(\text{O})\text{CH}_2\text{OH}$, 91948-78-6; $^-\text{O}_2\text{C}$ - p - $\text{C}_6\text{H}_4\text{N}(\text{O})\text{CH}_2\text{OH}$, 91948-79-7; $\text{PhN}(\text{O})\text{CH}_2\text{OH}$, 91948-80-0; Me - p - $\text{C}_6\text{H}_4\text{N}(\text{O})\text{CH}_2\text{OH}$, 91948-81-1.

(30) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(31) See, e.g.: (a) Albery, W. J. *Annu. Rev. Phys. Chem.* **1980**, *31*, 227.

(b) Murdoch, J. R.; Magnoli, D. E. *J. Am. Chem. Soc.* **1982**, *104*, 3792.

(32) Exner, O. In "Correlation Analysis in Chemistry", Chapman, N. B., Shorter, J., Eds.; Plenum Press: New York, 1978; p 439.