Methyl Radical Addition to Nitroalkane *aci*-Anions in Aqueous Solution: Rate Constants and Optical Absorption Spectra

By **Dieter Veltwisch** and **Klaus-Dieter Asmus**,* Hahn-Meitner-Institut für Kernforschung Berlin GmbH, Bereich Strahlenchemie, Postfach 39 01 28, D-1000 Berlin 39, Federal Republic of Germany

Absolute rate constants have been measured for the $^{\cdot}CH_3$ radical addition to the *aci*-anions of nitromethane, nitro-ethane, 1-nitropropane, and 2-nitropropane. The respective values of $(1.35 \pm 0.2) \times 10^8$, $(1.60 \pm 0.3) \times 10^7$, $(1.35 \pm 0.3) \times 10^7$, and $(2.35 \pm 0.5) \times 10^6$ dm^3 mol^{-1} s^{-1} indicate a nucleophilic character of the methyl radical. From Taft's relationship on the inductive substituent effect, $\rho^* + 8.9$ is derived. The optical absorption spectra of the methyl radical adducts, $R^1R^2CH_3NO_2^{\cdot-}$, are characterized by λ_{max} 270 nm and extinction coefficients of $(2.8—3.0) \times 10^3$ dm^3 mol^{-1} cm^{-1}.

ALKYL radicals usually exhibit considerably lower reactivities towards substrates than the majority of other radicals. Typical rate constants which have been measured for methyl radicals, for example, are found to be in the range of 10^3 dm^3 mol^{-1} s^{-1} for hydrogen abstraction reactions [1,2] or $10^3—10^6$ dm^3 mol^{-1} s^{-1} for addition to olefins.[1] Some higher values were reported for the addition to *p*-benzoquinone (k 4.5 × 10^7 dm^3 mol^{-1} s^{-1}) [3] and in particular for their reactions with O_2 and I_2 which occur almost diffusion controlled with k 4.7 × 10^9 and 6 × 10^9 dm^3 mol^{-1} s^{-1}, respectively.[1] Most often, however, the fast competing combination (1) which occurs

$$2 \, ^{\cdot}CH_3 \longrightarrow C_2H_6 \qquad (1)$$
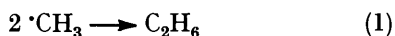
with $2k = (2.5—3.2) \times 10^9$ dm^3 mol^{-1} s^{-1} [4,5] dominates over a possible reaction of a methyl radical with other substrates in a given system.

In this paper we report some absolute rate constants for the addition of methyl radicals to nitroalkane *aci*-anions and the optical absorption spectra of these adducts. The data have been obtained by pulse radiolysis techniques. *aci*-Nitroalkane anions, $>C=NO_2^-$, are known to be good radical traps and are frequently used in e.s.r. experiments.[2,6,7] The latter could provide, however, only rough estimates of the order of 10^7 dm^3 mol^{-1} s^{-1} for the rate constants of the methyl radical addition process.[2] Optical absorption spectra have been reported for $^{\cdot}OH$ radical adducts to *aci*-nitroalkane anions and e_{aq}^- adducts to nitroalkanes with maxima slightly below 300 nm.[8,9]

A convenient source for methyl radicals is the $^{\cdot}OH$ radical reaction with dimethyl sulphoxide.[10,11] This reaction proceeds via diffusion controlled (k 1.0 × 10^{10} dm^3 mol^{-1} s^{-1}) addition and subsequent carbon–sulphur bond cleavage (k 1.5 × 10^7 s^{-1}) [reaction (2)] [11] to yield equal amounts of methyl radicals and sulphinic acid.

$$^{\cdot}OH + (CH_3)_2SO \longrightarrow (CH_3)_2SO(OH)^{\cdot} \longrightarrow$$
$$^{\cdot}CH_3 + CH_3SO_2^-/H^+ \qquad (2)$$
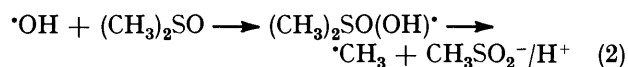
EXPERIMENTAL

Solutions were prepared from commercial compounds of highest available purity. The latter was checked by chromatographic methods and if necessary purification to $\gtrsim 99\%$ was achieved by standard distillation methods. The solvent was deionized, Millipore-filtered water.
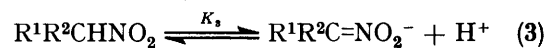
Solutions were deoxygenated by bubbling with N_2 (*ca.* 30 min for 1 dm^3 solution) and subsequently saturated (*ca.* 30 min) with N_2O. The latter was passed through a copper catalyst (BASF R3-11) and Oxisorb (Messer-Griesheim) to remove possible traces of oxygen. The N_2O was added to convert hydrated electrons, which are formed with about equal yield as $^{\cdot}OH$ radicals upon irradiation of an aqueous system, also into $^{\cdot}OH$ radicals via $N_2O + e_{aq}^- + H_2O \longrightarrow N_2 + OH^- + {}^{\cdot}OH$. The total yield of $^{\cdot}OH$ radicals in irradiated, N_2O-saturated solutions thus amounts to *ca.* 0.6 μmol J^{-1} absorbed energy (G *ca.* 6 species per 100 eV absorbed energy). The only other highly reactive species formed is the hydrogen atom whose yield is, however, only one tenth of the combined e_{aq}^-–$^{\cdot}OH$ yield.

Irradiations were carried out using pulse radiolysis techniques. Generally, short pulses of 0.5—2.0 μs duration of high energy electrons from a 1.55 MeV Van de Graaff generator were applied to the solutions. The dose per 1 μs pulse was *ca.* 6 J kg^{-1} (6 Gy or 600 rad) corresponding to *ca.* 3.6 × 10^{-6} mol dm^{-3} of $^{\cdot}OH$ radicals in the N_2O-saturated solutions.

Dosimetry was based on the reduction of tetranitromethane in N_2-saturated solutions of 10^{-3} mol dm^{-3} $C(NO_2)_4$ and 10^{-1} mol dm^{-3} propan-2-ol. Details on the experimental arrangements, dosimetry and evaluation of data have been published already.[12] All experiments were carried out at room temperature. Experimental limits of error are estimated to $\pm 10\%$ unless otherwise noted.

RESULTS AND DISCUSSION

Since nitroalkanes are known to exist in the tautomeric and acid–base equilibria (3) and (4) [13] and radical

$$R^1R^2CHNO_2 \underset{}{\overset{K_3}{\rightleftharpoons}} R^1R^2C=NO_2^- + H^+ \qquad (3)$$

$$R^1R^2C=NO_2H \underset{}{\overset{K_4}{\rightleftharpoons}} R^1R^2C=NO_2^- + H^+ \qquad (4)$$

addition takes place only at the C=N double bond, *i.e.* with the *aci*-form, the experiments were generally carried out at a pH > pK_3. The respective pK_3 range from 10.3 to 7.7 is going from CH_3NO_2 over $C_2H_5NO_2$, n-$C_3H_7NO_2$, to iso-$C_3H_7NO_2$ while the respective pK_4 values increase from 3.0 to 5.1 for the *aci*-nitroalkane acid–base equilibrium of the same series of compounds. Thus the conversion of the nitroalkane form into its *aci*-form requires a more or less basic environment and essentially yields only the respective *aci*-nitroalkane anions.

In pulse-irradiated, N_2O-saturated solutions of 10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 5×10^{-4} mol dm^{-3}-nitromethane at pH 11.1 the formation of a relatively long lived (>500 μs) optically absorbing species can be observed. Its absorption spectrum is shown in Figure 1 and is characterized by a maximum at 270 nm. Almost identical or at
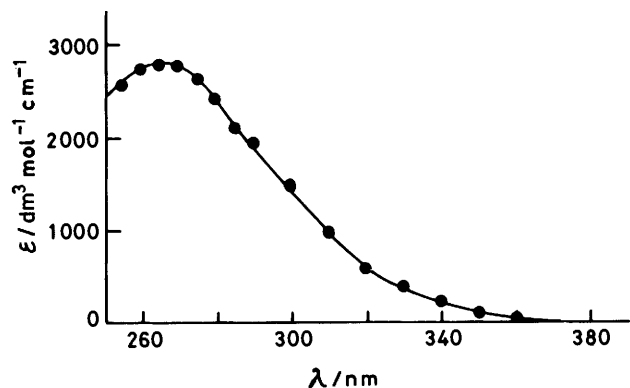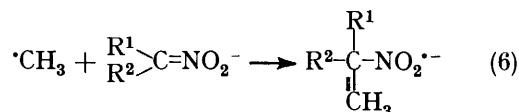
FIGURE 1 Optical absorption spectrum of $CH_3CH_2NO_2^{\cdot-}$ obtained from $^{\cdot}CH_3$ radical addition to $H_2C=NO_2^-$ in a pulse-irradiated solution of 10^{-1} mol dm^{-3}-$(CH_3)_2SO$ and 5×10^{-4} mol dm^{-3}-nitromethane at pH 11.1

least very similar spectra are known for the electron adduct to nitromethane, $CH_3NO_2^{\cdot-}$,[9] and the $^{\cdot}OH$ radical adduct to aci-nitromethane anions, $CH_2(OH)NO_2^{\cdot-}$,[8] which exhibit maxima at 270 and 280 nm, respectively. The transient absorption is therefore assigned to the methyl radical adduct formed in reaction (5). The

$$^{\cdot}CH_3 + H_2C=NO_2^- \longrightarrow \underset{\underset{CH_3}{|}}{H_2C}\text{-}NO_2^{\cdot-} \qquad (5)$$
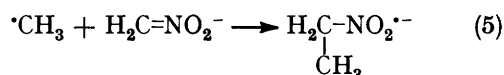
extinction coefficient of this radical anion at 270 nm is calculated as ε (2.8 ± 0.3) × 10^3 dm^3 mol^{-1} cm^{-1} on the basis of a $^{\cdot}CH_3$ yield of 0.56 μmol J^{-1} absorbed energy in reaction (2) and a quantitative addition reaction (5).

2-nitropropane as $^{\cdot}CH_3$ radical traps. The optical absorption spectra of the transient nitroalkane radical anions formed in general reaction (6) all exhibit the same

$$^{\cdot}CH_3 + \underset{R^2}{\overset{R^1}{>}}C=NO_2^- \longrightarrow \underset{\underset{CH_3}{|}}{R^2\text{-}\overset{\overset{R^1}{|}}{C}}\text{-}NO_2^{\cdot-} \qquad (6)$$

$\lambda_{max.}$ at 270 nm and practically the same extinction coefficients as can be seen from the Table.

Significant differences are observed for the bimolecular rate constants for the methyl radical addition to the nitroalkane aci-anions. Going from nitromethane to 2-nitropropane the respective k values are seen to
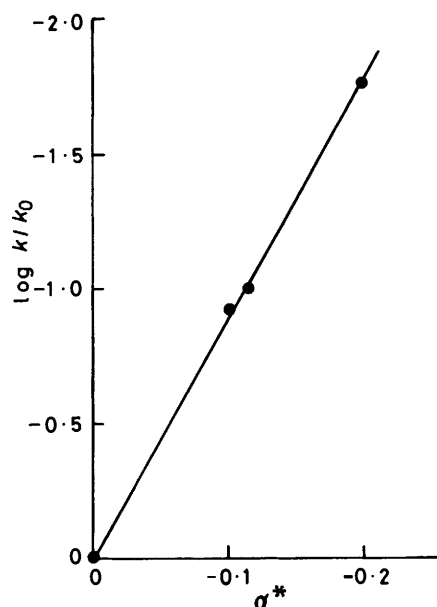
FIGURE 2 Plot of log k/k_0 versus Taft's σ^* induction constants (k_0 refers to $^{\cdot}CH_3$ addition to $H_2C=NO_2^-$)

Optical and kinetic data on various nitroalkane radical anions and their formation. Estimated error limits for $\lambda_{max.}$ ± 5 nm

$$\underset{\underset{CH_3}{|}}{R^2\text{-}\overset{\overset{R^1}{|}}{C}}\text{-}NO_2^{\cdot-}$$

R¹	R²	$\lambda_{max.}$/nm	ε/dm³ mol⁻¹ cm⁻¹	$k(CH_3^{\cdot} + \underset{R^2}{\overset{R^1}{>}}C=NO_2^{\cdot-})$/ dm³ mol⁻¹ s⁻¹	pH
H	H	270	(2.8 ± 0.3) × 10³	(1.35 ± 0.2) × 10⁸	11.1
H	CH₃	270	(3.0 ± 0.3) × 10³	(1.60 ± 0.3) × 10⁷	10.6
H	C₂H₅	270	(2.9 ± 0.3) × 10³	(1.35 ± 0.3) × 10⁷	10.7
CH₃	CH₃	270	(2.8 ± 0.5) × 10³	(2.35 ± 0.5) × 10⁶	10.7

The growth of the $CH_3CH_2NO_2^{\cdot-}$ absorption occurs exponentially with a half-life of 10μs. Variation of the nitromethane concentration results in the expected inverse proportionality between half-life and concentration, and from the kinetic data a bimolecular rate constant of k (1.35 ± 0.2) × 10^8 dm^3 mol^{-1} s^{-1} has been derived for reaction (5).

The same kind of experiment has also been conducted using the aci-anions of nitroethane, 1-nitropropane, and

decrease by two orders of magnitude and in any case indicate a process which is not diffusion controlled. In the case of 2-nitropropane, already relatively high solute concentrations of up to 10^{-2} mol dm^{-3} have to be applied in order for reaction (5) to compete successfully with the methyl radical combination [reaction (1)]. Under these conditions some of the hydrated electrons formed initially in the irradiation process will not be scavenged by the N_2O but can directly react with the aci-nitroalkane to

yield the corresponding $R^1R^2CHNO_2^{\cdot-}$ radical anion.[8] This process occurs, however, much faster than the methyl radical addition and can thus be well separated from reaction (6).

The trend in the kinetic data suggests a considerable influence of the inductive effect of R^1 and R^2 on the rates of reaction. Using Taft's σ^* constants for the inductive effect [14] the data can be described by equation (7)

$$\log k/k_0 = \rho^*\sigma^* \qquad (7)$$

with k_0 referring to the case where $R^1 = R^2 = H$. A corresponding plot is shown in Figure 2. From the slope of the straight line $\rho^* + 8.9$ is derived. The positive sign of ρ^* clearly indicates a nucleophilic character of the methyl radical. This is in accord with, for example, corresponding findings for the alkyl radical addition to olefins.[15] The absolute value of ρ^* is, of course, also likely to include steric effects on the rate of the methyl radical addition to the aci-anions of nitroalkanes.

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