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THE PHOTOCHEMICAL REACTION OF CERIUM(IV) AMMONIUM NITRATE WITH ALKENES. RATE AND MECHANISM FOR THE ADDITION OF THE NITRATE RADICAL TO ALKENES

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Abstract - The photochemical reaction of cerium(IV) ammonium nitrate (CAN) in acetonitrile with cyclohexene, 1-octene and a series of styrene derivatives leads to the formation of 1,2-dinitrate adducts in high yields. The reaction takes place by the intermediacy of the nitrate radical which forms in the photolysis of CAN. The reaction rate of $NO_3\cdot$ with the olefinic substrates has been determined by the laser flash photolysis technique. High values of reactivity are observed, the second order rate constants ranging from 5×10^8 to 9×10^9 $M^{-1}s^{-1}$. The plot of the rate data for substituted styrenes against σ^+ values is linear and affords a ρ value of -0.97. It has also been found that the kinetic data fit in with the Rehm-Weller equation for electron transfer processes, thus suggesting that the transfer of an electron from the substrate to the attacking radical is the first (and rate determining) step in the reaction of styrene derivatives with $NO_3\cdot$. This suggestion is also supported by the observation that trans-β-methylstyrene is more reactive than α-methylstyrene, in line with the easier oxidizability of the former substrate and in contrast with what is observed in free radical additions. Kinetic data for 1-octene and cyclohexene do not fit the Rehm-Weller plot and the mechanistic attribution to the reaction of these substrates with nitrate radical is uncertain.

It is now generally accepted that the role of one electron transfer processes in organic chemistry is much greater than it was thought in the past[1]. There is therefore considerable interest for studies aimed at distinguishing electron transfer steps from other possible reaction pathways, a distinction which nowadays has become of fundamental importance for a large number of organic reactions[2-6].

Reactions of free radicals with alkenes certainly belong to this category. Radical mechanisms for the addition to the double bond or for the abstraction of allylic hydrogens are still considered the most probable ones[7]. However, the involvement of electron transfer steps has recently been suggested in the reactions of alkenes with the charged radicals $Cl_2^{\bar{\cdot}}$ and $SO_4^{\bar{\cdot}}$ [6,8,9], and with ClO_2[10].

Recently, we have investigated the reactions of the nitrate radical with alkanes and alkylaromatic compounds[11,12]. The experimental results have indicated that NO_3 reacts with alkanes by a H-atom transfer mechanism, as expected. However, with alkylaromatic compounds more easily oxidizable than toluene, results have suggested an electron transfer mechanism.

The capability of the nitrate radical to act as one electron oxidant, even when it can be involved in the H-atom transfer step, is certainly noteworthy. It is therefore seemed worthwhile to extend our study to the reaction of $NO_3\cdot$ with olefinic substrates since in this case too electron transfer could compete with radical addition. Information on this competition is certainly relevant to a deeper understanding of the scope of electron transfer processes in organic chemistry. Moreover, such information should improve our knowledge of the properties of the nitrate radical, which is of current interest in view of the role that this radical plays in several pollution phenomena. Indeed, several studies concerning the reactivity of the nitrate radica with a variety of organic compounds, both in the gas and in the liquid phase, have recently appeared in the literature[13,14], but none have specifically dealt with the mechanistic aspect of the processe involved.

In this paper we report on the light-induced reaction of cerium(IV) ammonium nitrate (CAN) with a series of styrene derivatives and with 1-octene and cyclohexene. Since under these conditions the effective reacting species is the nitrate radical[12], we have carried out a kinetic study of the reaction of this radical with the various alkenes by the laser flash photolysis technique.

RESULTS

Recently it has been reported that the thermal reaction of cerium(IV) ammonium nitrate with alkenylaromatic compounds in acetonitrile leads to the formation of 1,2-dinitrate adducts[15,16]. We have found that the same reaction occurs at much faster rate when, at room temperature, the solution containing CAN and the substrate is irradiated by a high pressure mercury lamp (125W). Under these conditions good to high yields of dinitrates (60-100%) are obtained in all cases and the reaction can satisfactorily be extended to unactivated olefins, such as 1-octene and cyclohexene. The results are in Table 1.

Table 1 - Photochemical nitrooxylation of alkenes with CAN in CH_3CN at room temperature[a].

Substrate	Yield of dinitrate adduct,%[b]
styrene	86
3-chlorostyrene	61
4-chlorostyrene	73
4-methylstyrene	70
3-trifluoromethylstyrene	75
2,4-dichlorostyrene	95
α-methylstyrene	96
<u>trans</u>-β-methylstyrene	87[c]
<u>trans</u>-β-methylstyrene	- [d]
cyclohexene	60
1-octene	91[e]

[a] Substrate and CAN, $4x10^{-2}$M (125W, high pressure mercury lamp, reaction time 5-20 min).
[b] Yields with respect to CAN used, considering a CAN: alkene 2:1 stoichiometry, and determined by NMR analysis of the crude reaction product using p-dimethoxybenzene or bibenzyl as the internal standard. [c] The threo/erythro dinitrate ratio is <u>ca.</u> 0.5. [d] Thermal reaction. The reaction time (5 min) is the same as in the corresponding photochemical process. [e] Determined after reduction of the dinitrates to the corresponding diols by $LiAlH_4$.

The beneficial effects of light is shown by the observation that the photochemical reaction of trans-β-methylstyrene with CAN leads to 87% of dinitrate adduct whereas, in the absence of light, no product is observed in the same reaction time (5 min). As the thermal one, also the photochemical process exhibits a 2:1 CAN:substrate stoichiometry. Accordingly, the quantum yield of the photochemica process (styrene as the substrate) is 1.2 with resepct to CAN and 0.61 with respect to the alkene.

Another interesting observation is that no significant formation of allylic substitution products is observed in the reactions of substrates with allylic hydrogen atoms. In view of the analytical method used, the yield of these products, if formed, is certainly less than 5%.

When the photolysis of CAN is carried out by the laser flash (JK System 2000 ruby laser, λ_{exc}=347nm)[17] the formation of a transient whose spectral properties correspond to those of the nitrate radical is observed[18] (see Experimental). We have also found that the addition of an olefinic substrate causes a significant increase in the decay rate of the nitrate radical, the extent of which depends upon the structure of the olefin. There is therefore little doubt that the formation of dinitrates in the photochemical reaction of CAN with olefins in acetonitrile can be accounted for by the mechanism described in Scheme 1.

$$Ce^{IV}ONO_2 \xrightarrow[(1)]{h\nu} Ce^{III} + NO_3\cdot$$

$$RCH{=}CH_2 + NO_3\cdot \xrightarrow[(2)]{} R\dot{C}HCH_2ONO_2$$

$$Ce^{IV}ONO_2 + R\dot{C}HCH_2ONO_2 \xrightarrow[(3)]{} RCH(ONO_2)CH_2ONO_2 + Ce^{III}$$

Scheme 1

Once the β-nitrate radical is formed (step 2), its conversion into the dinitrate adduct (step 3) very propably occurs by an oxidative ligand transfer mechanism, in view of the strong tendency of CAN to be involved in such type of processes[19].

The kinetics of the reaction were studied by subjecting an acetonitrile solution, $2x10^{-4}$M in CAN and $2x10^{-4}$M in the olefinic substrate, to the laser flash at the temperature of 23 ± 1°C and following the decay of $NO_3\cdot$ at 630 nm. With respect to the concentration of the formed $NO_3\cdot$ the alkene was always in significant excess (at least 10 times) and first order plots of satisfactory linearity were obtained by which the second order rate constants (k) reported in Table 2 were obtained as usual. No trend in the k values with the substrate concentration was observed and the effect of added salts (Me_4NClO_4 or Et_4NNO_3) was insignificant. Rates were also the same, within experimental errors, in deareated solutions. A spontaneous decay of the nitrate radical in acetonitrile was also observed. However, under the conditions of our experiments the rate of this spontaneous reaction was always at least 10 times slower than that found in the presence of the olefinic substrates.

DISCUSSION

The kinetic data reported in Table 2 refer to step 2 of Scheme 1 and therefore give informatio on the reactivity of $NO_3\cdot$ towards the olefinic substrates. Clearly, this radical exhibits a very high reactivity, k values spanning from 5×10^8 to $9\times10^9 M^{-1}s^{-1}$, the latter value being very close to that of a diffusion controlled reaction (*ca.* 2×10^{10} $M^{-1}s^{-1}$, in acetonitrile).

Table 2 - Second order rate constants for the reaction of $NO_3\cdot$ with alkenes in CH_3CN at room temperature.

Substrate[a]	k, $M^{-1}s^{-1}$ [b]
styrene	3.9×10^9
4-methylstyrene	7.0×10^9
4-chlorostyrene	3.3×10^9
3-chlorostyrene	1.8×10^9
3-trifluoromethylstyrene	9.6×10^8
2,4-dichlorostyrene	1.4×10^9
α-methylstyrene	5.1×10^9
trans-β-methylstyrene	8.9×10^9
cyclohexene	2.7×10^9
1-octene	4.9×10^8

[a] Substrate, $2\times10^{-4}M$. [b] Mean values of at least three determinations (error ± 10%). [c] The same value, within experimental error, was obtained in the presence of Et_4NNO_3, $1\times10^{-2}M$, in the presence of Me_4NClO_4, $1\times10^{-2}M$, and at the substrate concentrations 3×10^{-4}, 4×10^{-4} and $5\times10^{-4}M$.

Concerning the detail mechanism of the process, the main question to be answered is whether the nitrate radical directly adds to the double bond or if it, first, abstracts an electron from the substrate forming a radical cation (eq. 1), which subsequently reacts with NO_3^- to give te β-nitrate radical (eq. 2). The latter two-step process deserves carefull consideration in view of the oxidizin power of the nitrate radical (2.1-2.4V *vs.* SCE, in water[14]) and the already mentioned behaviors

$$RCH{=}CH_2 + NO_3\cdot \longrightarrow R\overset{+}{C}H\text{-}\overset{\cdot}{C}H_2 + NO_3^- \qquad (1)$$

$$R\overset{+}{C}H\text{-}\overset{\cdot}{C}H_2 + NO_3^- \longrightarrow R\overset{\cdot}{C}HCH_2ONO_2 \qquad (2)$$

shown by this radical in the reaction with alkylaromatic compounds[12].

A first information with respect to this mechanistic problem may be provided by the intermolecul selectivity of the process, which can be determined by the Hammett plot for a series of substituted styrenes, using the σ^+ constants. A satisfactory linear correlation with σ^+ values is obtained

(Fig. 1), from which a ρ value of -0.97 is calculated. It can also be noted that all substrates lie on the same line, suggesting that the reaction mechanism remains unchanged along the entire series[20]

The low selectivity might indicate a free radical mechanism since very low values are generally observed in free radical reactions. However, in view of the high reactivity of the system, a small intermolecular selectivity can be consistent as well with a near diffusion controlled electron transfer. Indeed, a ρ value, as small as -0.56, has recently been determined for the TiO_2 catalyzed photooxidation of 1,1-diarylethenes, a reaction which nevertheless has been suggested to occur by an electron transfer mechanism[21]. In this respect, it is also worthwhile to note that in the free radical addition of benzenethiyl radicals to styrenes the ρ value is significantly smaller than that observed here, even though the reactivity of the benzenethiyl radical is two order of magnitude lower than that of the nitrate radical[22].

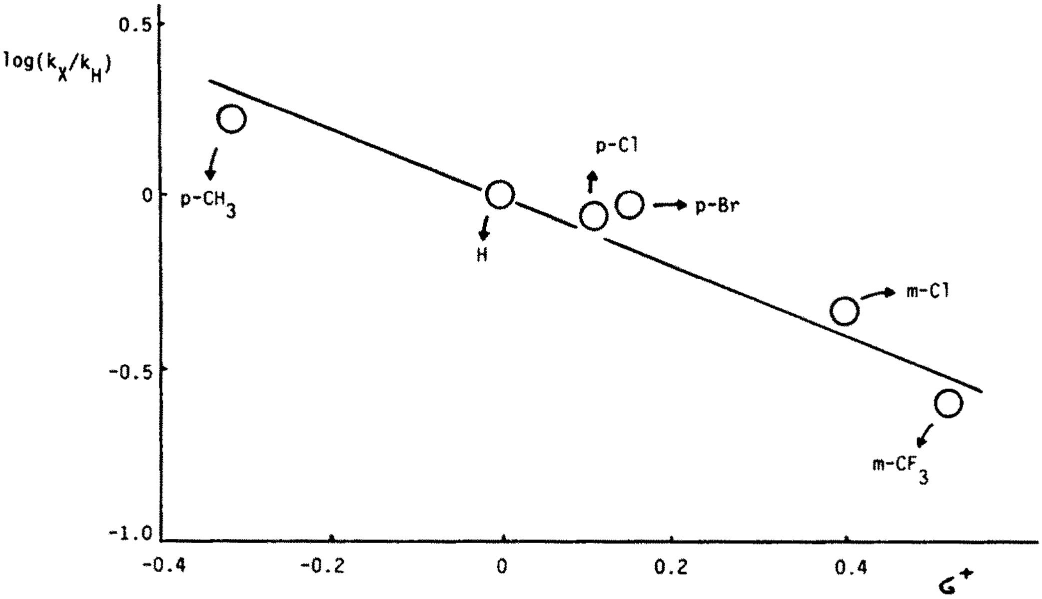

Fig. 1 - Correlation between relative reactivities ($\log k_X/k_H$) of substituted styrenes ($XC_6H_4CH{=}CH_2$) and substituent constants (σ^+) for the reaction with $NO_3\cdot$.

Support to an electron mechanism comes from the finding that <u>trans</u>-β-methylstyrene is more reactive that α-methylstyrene, in line with the easier oxidizability of the former substrate [23]. In contrast, the reverse order is generally observed for free radical additions with electrophilic radicals, as expected on the basis of steric and polar effects. Thus, with benzenethiyl radicals, α-methylstyrene is <u>ca.</u> 10 times more reactive than <u>trans</u>-β-methylstyrene[22,24], and a reactivity ratio of <u>ca.</u> 5 is observed with trichloromethyl radicals[25]. Interestingly, <u>trans</u>-β-methylstyrene has been found to be more reactive than α-methylstyrene in the reaction with ClO_2[10], a reaction thought to occur by an electron transfer mechanism.

It is widely recognized that a very significative test for the operation of an electron transfer mechanism can be found into the framework of the Marcus[26] and Rehm-Weller[27] theories, which predict the existence of well defined relationships between reaction rates and free energy changes in electron transfer processes. Unfortunately, a rigorous use of this test is not possible in our case since the standard oxidation potentials (E°) for the olefins under investigation are unknown and their measurements is made extremely difficult by the high degree of irreversibility of the oxidation process of these substrates. Thus we cannot know the precise value of the free energy changes involved in the transfer of an electron from the alkene to the nitrate radical.

However, the problem can be circumvented, at least to a first approximation, by means of the correlations which generally exist between the E° values and other more easily accessible parameters[2 As a matter of fact, a fair correlation exists (Fig. 2) between the E° values of methylbenzenes and the hν values (eV) of the charge transfer (CT) complexes that they form with tetracyanoethylene (TCN This relationship is given by equation 3 (r=0.945).

$$E^\circ = 0.91(h\nu)_{CT} - 0.61 \qquad (3)$$

If now we assume that also the alkenylaromatic compounds fit in with this correlation, it becomes possible to calculate approximate E° values (*vs.* SCE) for these compounds using their $(h\nu)_{CT}$ values measured as described in the Experimental Part (Table 3). The assumption that alkenyl- and alkylaromatics follow the same $(h\nu)_{CT}/E^\circ$ correlation is reasonable since it has already been observed that both kinds of substrates fit in with the same ionization potential *vs.* oxidation potential correlation[31]. Moreover, they lie on the same Rehm-Weller curve in the electron transfer fluorescence quenching of cyanosubstituted anthracenes[32].

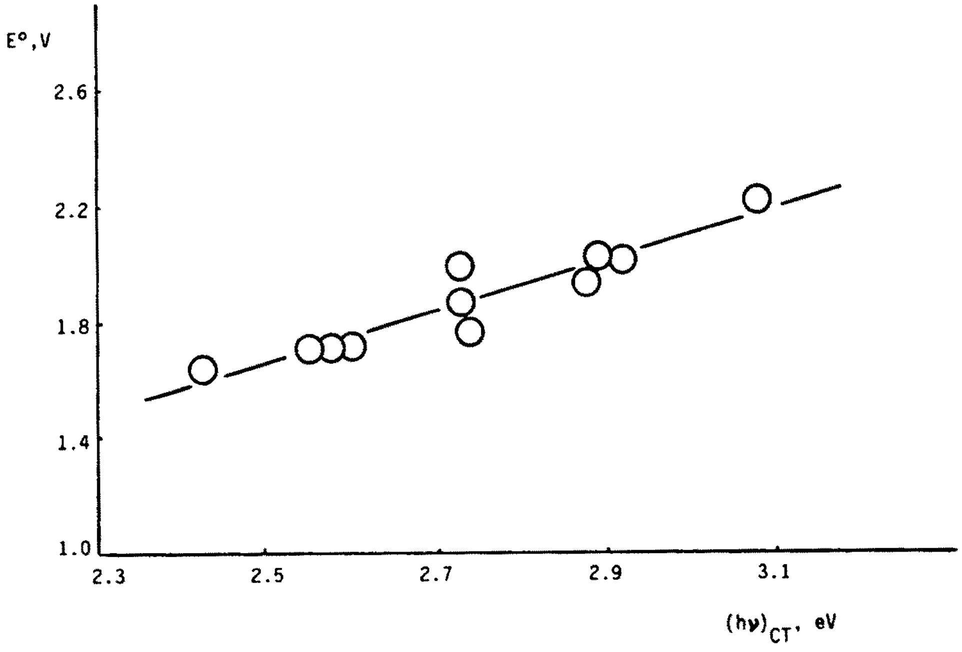

Fig.2 - The correlation of standard oxidation potential (E°) of methylbenzenes (from toluene to pentamethylbenzene) with the transition energies, $(h\nu)_{CT}$, for the CT complexes with TCNE. E° values (*vs.* SCE) from C.J. Schlesener et al., *J. Phys. Chem.*, *90*, 3747 (1986), $(h\nu)_{CT}$ values in CCl_4 from R.K. Chan, S.C. Liao, *Can. J. Chem.*, *48*, 299 (1970). The E° values have been corrected for transfer from trifluoroacetic acid to acetonitrile according to C.J. Schlesener et al., *J.Am. Chem. Soc.*, *106*, 3567 (1984).

Thus, the $\Delta G^{\circ\prime}$values (in kcal mol^{-1}) for the transfer of an electron from the alkene to $NO_3\cdot$ (eq. 1) can be calculated by equation 4, where $E^\circ_{NO_3\cdot/NO_3^-}$ is 2.0 V *vs.* SCE[12], the E° values for alkenes are those in Table 3 and $e^2/a\varepsilon$ is the energy obtained by bringing the alkene radical cation

$$\Delta G^{\circ\prime} = 23.06\,\left(E^{\circ}_{\mathrm{alkene}} - E^{\circ}_{\mathrm{NO_3\cdot/NO_3^-}} - \frac{e^2}{a\varepsilon}\right) \qquad (4)$$

and NO_3^- to encounter distance (e = electronic charge, a = internuclear distance in the collision complex, ε =dielectric constant of the solvent)[29,30]. The value of $e^2/a\varepsilon$ in our case is 0.08 eV ($a = r_{\mathrm{alkene}} + r_{\mathrm{NO_3\cdot}} = 3.5 + 1.2 = 4.7$ Å; $\varepsilon_{\mathrm{MeCN}} = 37.5$).

In Fig. 3 the logarithms of k values (Table 1) are plotted against the $\Delta G^{\circ\prime}$ values, calculated as described. It can be seen that the kinetic data for styrenes fit in reasonably well with the theoretical line derived from the Rehm-Weller equation[27], which correlates the rate costants for an electron transfer reaction with the free energy changes in the electron transfer equilibrium.

Table 3 - Charge transfer transition energies, $(h\nu)_{CT}$, and calculated E° values for a series of styrenes.

Substrate	$(h\nu)_{CT}$,eV[a]	E°,V[b]
1. 3-trifluoromethylstyrene	2.88	2.01
2. 2,4-dichlorostyrene	2.72	1.86
3. α-methylstyrene	2.60	1.76
4. styrene	2.59	1.75
5. 3-chlorostyrene	2.56	1.72
6. 4-chlorostyrene	2.49	1.65
7. 4-methylstyrene	2.38	1.55
8. *trans*-β-methylstyrene	2.36	1.54

[a] Values for charge transfer complexes with tetracyanoethylene in CCl_4 determined as described in Experimental. [b] Values *vs.* SCE in CH_3CN calculated from equation 3.

This equation refers to a kinetic sequence reported in Scheme 2 where a diffusion controlled encounter of A (acceptor = oxidant) and D (donor = reductant) to form the precursor complex occurs reversibly in the first step (k_d and k_{-d}). This complex undergoes a reversible electron transfer (k_{el} and k_{-el}) leading to a successor complex which, finally, forms the free species A^- and D^+ by an irreversible reaction (k_p).

$$A + D \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} (A....D) \underset{k_{-el}}{\overset{k_{el}}{\rightleftarrows}} (A^{\bar{\cdot}}\quad D^{\dot{+}}) \xrightarrow{\quad k_p \quad} A^{\bar{\cdot}} + D^{\dot{+}}$$

Scheme 2

The best fit is obtained with a reorganization energy (λ) of 20 kcal mol^{-1}, corresponding to an intrinsic barrier $\Delta G^{\neq}(0)$ of 5 kcal mol^{-1}, identical to that recently found for the reaction of NO_3 with alkylaromatics[12].

Thus, even though with the caution imposed by the approximations previously discussed, the resul of this test can be considered to support an electron transfer mechanism, in line with the other evidence shown above.

Much more uncertain is the mechanistic attribution for the reactions of the unactivated alkenes: 1-octene and cyclohexene. If these substrates too are supposed to follow eq. 3, E° values of 2.08 and 2.61 V are obtained for cyclohexene and 1-octene, respectively, from the measured $(h\nu)_{CT}$ values (2.95 eV for cyclohexene and 3.54 eV for 1-octene). However, both substrates do not fit the theoretic plot of Fig. 3 since their reactivity is significantly higher than that predicted from the plot, expecially for the case of 1-octene ($\Delta G^{\circ\prime}$ is *ca.* 0 kcal mol^{-1} for cyclohexene and 12.2 kcal mol^{-1} for 1-octene).

Certainly, it is possible that cyclohexene and, particularly, 1-octene react by a mechanism (presumably free radical addition) different from that of styrenes, but it cannot be excluded that th observed deviations from the plot are simply due to the fact that the two unactivated alkenes belong to a different reaction series with, for instance, a lower intrinsic barrier than that of alkenylarom Moreover, it may also be that a satisfactory use of equation 3 for the calculation of E° is restricte to alkenylaromatic compounds.

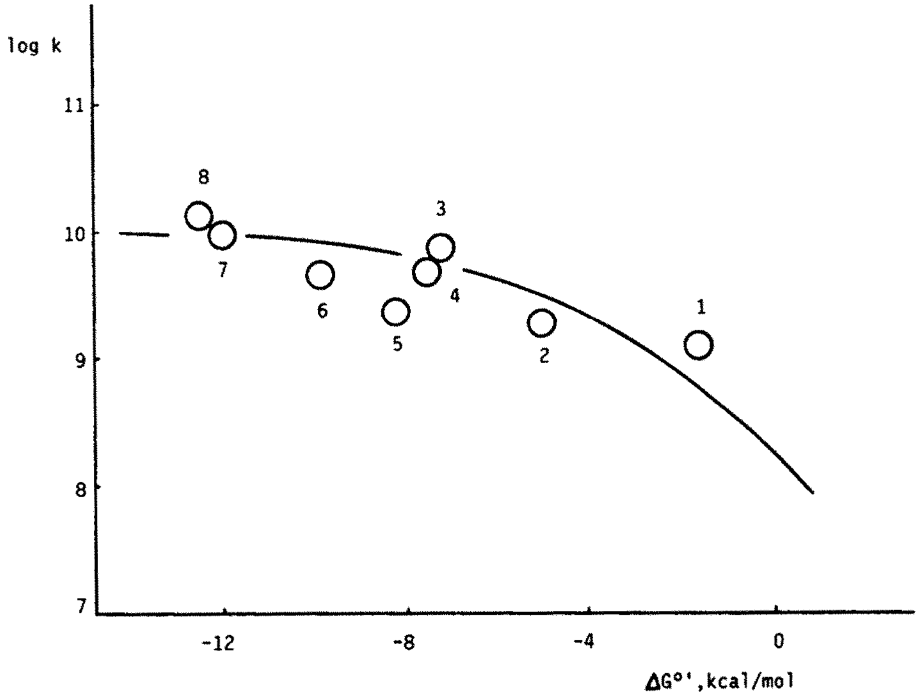

Fig. 3 - Plot of log k *vs.* $\Delta G^{\circ\prime}$ for the reaction of $NO_3\cdot$ with styrenes. The curve was calculated[27] usi the following values (Scheme 2) $k_d = k_{-d} = 1x10^{10}\ M^{-1}s^{-1}$, $Z = 6x10^{11}\ s^{-1}$, and $k_p = 1x10^{10}\ s^{-}$ For the numbering see Table 3.

EXPERIMENTAL

^{1}H NMR spectra were taken on a Bruker WP 80 CW spectrometer. IR and UV spectra were recorded on a Perkin-Elmer 257 and Perkin-Elmer 551S spectrophotometer, respectively. VPC analyses were performed on a 558A Hewlett-Packard gaschromatograph. The laser flash photolysis experiments were carried out with the JK System 2000 pulsed ruby laser previous described[17].

Materials - Ceric ammonium nitrate, $(NH_4)_2Ce(NO_3)_6$, was dried at 85 °C for 1 h before the use. 2,4-Dichlorostyrene was prepared by dehydration of 2,4-dichlorophenylmethylcarbinol as reported[33].

3-Trifluoromethylstyrene was obtained by dehydration of 3-trifluoromethylphenethyl alcohol as described[34]. All the other alkenes were commercial samples distilled before use. For laser photolysis experiments, acetonitrile HPLC grade was used.

Photooxidation procedure and reaction stoichiometry - The solution of the substrate (4 mmol) and CAN (4 mmol) in CH$_3$CN (100 ml) was irradiated by an immersion high pressure mercury lamp (Helios Italquartz, 125W) with pyrex jacket, at room temperature, until the separation of a white solid, Ce(III) salt, from the pale yellow solution. UV spectrophotometric analysis of a small portion of the solution showed that CAN was practically absent ($\sim$ 0.02 mmol). The reaction time was in a range of 5-20 min, depending on the substrate reactivity. The solvent was then evaporated at reduced pressure, the residue was extracted several times with n-hexane and the solvent again evaporated in the vacuum. By VPC analysis of the crude product on a capillary column (SP 2340), it was shown that only 2 mmol of substrate had reacted, thus indicating a 2:1 CAN:substrate stoichiometry.

Reaction products - Since dinitrates tend to decompose to a variable extent during separation procedures, they were generally characterized by spectroscopic methods directly in the crude reaction product or after reduction to the corresponding diols. In the case of styrene and substituted styrenes (3-chloro, 4-chloro, 3-trifluoromethyl, 4-methyl, 2,4-dichloro) the crude product gave an IR spectrum (CHCl$_3$) exhibiting the characteristic peaks of the nitrate group at 1640 and 1280 cm^{-1}. Styrene and all the monosubstituted derivatives had the same NMR spectrum (CDCl$_3$) with signals at δ 7.2-7.6 (4 or 5H, m, ArH), 6.0 (1H, t, J=6Hz, $>$CHAr) and 4.6 (2H, d, J=6Hz, -CH$_2$-), which is in agreement with the ArCH(ONO$_2$)CH$_2$ONO$_2$ structure. The AX$_2$ system due to -CH(ONO$_2$)CH$_2$ONO$_2$, however, changed to an ABX system for the case of the dinitrate derived from 2,4-dichlorostyrene: δ 6.5 (1H, 4 peaks, X portion, $>$CHAr) and 4.7 (2H, 3 peaks, AB portion, -CH$_2$-). The crude products of the reaction of 4-chlorostyrene and 2,4-dichlorostyrene were also subject to column chromatgraphy on silica gel eluting with 9.5:0.5 n-hexane:diethyl ether mixture, and the isolated dinitrates analyzed by mass spectrometry (70 eV). The results (m/e, relative intensity) were as follows. 4-Chlorophenyl-1,2-ethanediol dinitrate: 262 (M$^+$, 100), 264 (M$^+$+2, 33), 2,4-dichlorophenyl-1,2-ethanediol dinitrate: 296 (M$^+$, 100), 298 (M$^+$+2, 67), in line with the proposed structure. In the case of the reaction of α-methylstyrene and 1-octene, the dinitrate adducts were converted into the corresponding diols by reduction with Zn/AcOH and by LiAlH$_4$, respectively: the diol from α-methylstyrene was characterized by comparison with literature data[35], that from 1-octene by comparison with an authentic specimen (commercial product).1,2-Cyclohexanediol dinitrate (mixture of *cis*- and *trans*-isomer) was identified by spectroscopic comparison with literature data[36]. The reaction of *trans*- β -methylstyrene gave a product whose NMR spectrum was consistent with a 1:2 mixture of threo- (comparison with an authentic specimen[16]) and erythro-1-phenyl-1,2-propanediol dinitrate (comparison with literature data[37]).

Visible spectrum of NO$_3\cdot$ in CH$_3$CN - Portions of a solution of CAN in CH$_3$CN, 2x10^{-4}M, were placed in a 5 cm long cylindrical quartz cell and irradiated using the doubled frequency (λ = 347 nm) of a pulsed ruby laser. For each portion the higher signal intensity of the oscilloscopic trace (after 1μs from the laser flash) at a fixed wavelength has been measured. Only one flash was made on each cell filling. By plotting the optical densities (calculated by signal intensities) *vs.* the corresponding wavelengths, the spectrum of the transient was obtained, which was that expected (maxima at λ= 595, 635, 673 nm) for the nitrate radical[38]. On the basis of its approximate extinction coefficient[38], the concentration of the generated nitrate radical should be *ca.* 1.5x10^{-5}.

Kinetics - A solution of the substrate, 2x10^{-4}M, and CAN, 2x10^{-4}M, in CH$_3$CN was placed in the cell and subject to the laser flash photolysis as before. Kinetics of the reaction of NO$_3\cdot$ was determined by monitoring the decay of its absorption at 630 nm. All measurements were carried out at room temperature (23 + 1°C). The decay of NO$_3\cdot$ in the presence of the excess of substrate followed a first order kinetic from which first order rate constants were calculated by using a linear least square treatment. The second order rate constants (Table 2), calculated as usual, were insensitive to changes in the substrate concentration. Moreover, no change in the reaction rate was observed when oxygen purged solutions were used.

Charge transfer spectra - Spectral measurements of the CT absorption band were carried out in a Perkin-Elmer 551S spectrophotometer by mixing solutions of alkenes (10^{-2} - 10^{-1}M) and tetracyanoethylene (10^{-4} - 10^{-3}M) in CCl$_4$. Only exception was 1-octene for which the solvent was CH$_2$Cl$_2$. In CCl$_4$ the CT absorption band for this substrate was too weak to be measured with reasonable precision.

Quantum yield measurements - Photochemical quantum yields were measured at 366 nm by means of a collimated HBO 200W medium pressure mercury arc and an interference filter. Potassium ferrioxalate was used as the actinometer. The concentration range used for the reagents was 5x10^{-4} - 1x10^{-3}M. The quantum yield determined by measuring the disappearance of CAN spectrophotometrically was 1.2, whereas the value obtained on the basis of the reacted substrate (gaschromatographic analysis) was 0.61, in line with the 2:1 CAN:substrate stoichiometry. The same value of quantum yield was obtained either when the CAN/substrate molar ratio was 1 or when it was 2.

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REFERENCES AND NOTES

1. L. Eberson, "Electron Transfer Reaction in Organic Chemistry", Springer-Verlag, Berlin (1987).
2. F.G. Bordwell, C.A. Wilson, J. Am. Chem. Soc., 109, 5470 (1987).
3. S. Hoz, M. Lirnch, D. Cohen, J. Am. Chem. Soc., 109, 5149 (1987).
4. E.C. Ashby, T.N. Pham, Tetrahedron Lett., 3183 (1987).
5. S. Fukuzumi, J.K. Kochi, J. Am. Chem. Soc., 103, 7240 (1981); 104, 7599 (1982).
6. M.J. Davies, B.C. Gilbert, J. Chem. Soc., Perkin Trans. 2, 1809 (1984).
7. P.I. Abel, in "Free Radicals", J.K. Kochi, Ed., Wiley Interscience: New York (1973) Vol. II, Chapter 13.
8. C. Arnoldi, A. Citterio, F. Minisci, J. Chem. Soc., Perkin Trans. 1, 531 (1983).
9. A. Citterio, C. Arnoldi, C. Giordano, G. Castaldi, J. Chem. Soc., Perkin Trans. 1, 891 (1983)
10. C.R. Acha, E. Choshen (Goldstein), S. Sarel, Helv. Chim. Acta, 69, 1728 (1986); E. Choshen (Goldstein), R. Elits, C.R. Acha, Tetrahedron Lett., 5989 (1986).
11. E. Baciocchi, T. Del Giacco, G.V. Sebastiani, Tetrahedron Lett., 1941 (1987).
12. E. Baciocchi, T. Del Giacco, S.M. Murgia, G.V. Sebastiani, J. Chem. Soc., Chem. Commun., 1246 (1987).
13. T.J. Wallington, R. Atkinson, A.M. Winer, J.N. Pitts, Jr., J. Phys. Chem., 90, 4640 (1986); R. Atkinson, W.P.L. Carter, C.N. Plum, A.M. Winer, J.N. Pitts, Jr., Int. J. Chem. Kinetics, 16, 887 (1984).
14. P. Neta, R.E. Huie, J. Phys. Chem., 90, 4644 (1986).
15. E. Baciocchi, C. Rol, G.V. Sebastiani, A. Zampini, J. Chem. Soc. Chem. Commun., 1045 (1982).
16. E. Baciocchi, C. Rol, G.V. Sebastiani, Gazz. Chim. Ital., 118, 285 (1988).
17. S.M. Murgia, A. Pasqua, A. Poletti, Chem. Phys. Lett., 98, 179 (1983); A. Poletti, S.M. Murgia, S. Cannistraro, Photobiochem. Photobiophys., 2, 167 (1981).
18. E. Baciocchi, T. Del Giacco, C. Rol, G.V. Sebastiani, Tetrahedron Lett., 541 (1985).
19. E. Baciocchi, C. Rol, L. Mandolini, J. Org. Chem., 42, 3682 (1977).
20. In the thermal reaction of CAN with alkenyl aromatics[15] the log k_X/k_H vs. σ^+ plot indicated a change of mechanism on passing from substrates with an ionization potential higher than that of styrene (which reacted by a radical mechanism) to substrates with an ionization potential lower than that of styrene (which reacted by an electron transfer mechanism). In this reaction, however, the oxidizing species is Ce(IV), so that situation can be different when the reacting species is $NO_3\cdot$ as in the presently studied photochemical process.
21. M.A. Fox, C. Chen, Tetrahedron Lett., 547 (1983).
22. O. Ito, M. Matsuda, J. Am. Chem. Soc., 104, 1701 (1982).
23. Actually, ionization potentials of α- and trans-β-methylstyrene are unknown. However, the easier oxidizability of the latter substrate is clearly deduced on the basis of the $h\nu$ values of their charge transfer complexes with tetracyanoethylene[15].
24. O. Ito, M. Matsuda, J. Org. Chem., 48, (1983).
25. J.I.G. Cadogan, I.H. Sadler, J. Chem. Soc. B, 1191 (1966).
26. R.A. Marcus, Ann. Rev. Phys. Chem., 15, 155 (1964).
27. D. Rehm, A. Weller, Isr. J. Chem., 8, 259 (1970).
28. Reliable E° values are known only for a limited number of compounds[29]. Thus, the indirect evaluation of approximate values of E° is frequently needed[30]. On the other hand the existence of nice correlations between oxidation potentials and charge transfer transition energies is long known. See E.S. Pysh, N.C. Yang, J. Am. Chem. Soc., 85, 212 (1963)
29. Ref. 1, p. 44.
30. L. Eberson, Adv. Phys. Org. Chem., 18, 79 (1982). See, in particular pp. 123-129.
31. L.L. Miller, G.D. Nordblom, T.A. Mayeda, J. Org. Chem., 37, 916 (1972). We could not use the E°/IP correlation since IP values for many substituted styrenes are unknown.
32. J. Eriksen, C.S. Foote, J. Phys. Chem., 82, 2659 (1978).
33. C.G. Overberger, J.H. Saunders, Org. Syn. Coll., Vol. 3, p. 204.
34. G.B. Bechman, L.L. Lewis, J. Am. Chem. Soc., 69, 2022 (1947).
35. J.E. Lynch, E.L. Eliel, J. Am. Chem. Soc., 106, 2943 (1984).
36. R.J. Ouellette, R.J. Bertsch, J. Org. Chem., 41, 2783 (1976).
37. D.W. Brixius, Ph.D. Thesis, Iowa State University (1972); Diss. Abs. Int. B.,33, 4722 (1973).
38. P.H. Wine, R.L. Mauldin, III, R.P. Thorn, J. Phys. Chem., 92, 1156 (1988).