^{15}N-CIDNP during Photonitration of Phenol with Tetranitromethane and Reactions with Nitric and Nitrous Acid

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Received September 29, 1997

Keywords: Radical reactions / Electron transfer / Nitration / Radical ions / Nitric oxides

During the irradiation of phenol (**1**) with ^{15}N-enriched tetranitromethane in acetonitrile, and during the reaction of **1** with ^{15}N-enriched nitric acid and nitrous acid, emission due to the nitration products *o*- and *p*-nitrophenol (**2a**, **2b**) is observed in the ^{15}N-NMR spectra. The CIDNP effects are built up by radical pairs formed by the encounters of the radicals $NO_2^{\bullet}$ and $\mathbf{1}^{+\bullet}$ or $PhO^{\bullet}$. During the reaction of **1** with nitrous acid, **2b** is formed, in part due to a non-radical reaction, via oxidation of *p*-nitrosophenol (**3**).

The nitration of aromatic compounds plays an important role in organic chemistry[1]. The mechanism for the nitration reaction depends on the nature of the nitrating system, the actual reaction conditions, and in many cases is still under discussion. In various nitration systems, nitronium ions NO_2^+ are involved as reaction intermediates. The discussion then focusses on the question as to whether the cationic intermediate (σ complex) is formed by addition of the nitronium ions NO_2^+ to the arenes (Eq. 1a), or by recombination of the radicals $NO_2^{\bullet}$ with arene radical cations (Eq. 1b)[2][3].

$$\begin{array}{llll} ArH + NO_2^+ & \rightarrow ArH^+{-}NO_2 & \rightarrow Ar{-}NO_2 + H^+ & (1a) \\ ArH^{+\bullet} + NO_2^{\bullet} & \rightarrow ArH^+{-}NO_2 & \rightarrow Ar{-}NO_2 + H^+ & (1b) \\ \quad \mathbf{1} & \quad (\sigma \text{ complex}) & \quad \mathbf{2} & \end{array}$$

1: Phenol; **2a**: *o*-Nitrophenol; **2b**: *p*-Nitrophenol

The radical cations $ArH^{+\bullet}$ might be formed via electron transfer (ET) between NO_2^+ and, if they are more reactive than toluene, arenes[4].

$$\text{ET: } ArH + NO_2^+ \rightarrow ArH^{+\bullet} + NO_2\bullet \qquad (2)$$

It has been shown by both CIDNP investigations and theoretical considerations that ET plays, if any, only a minor role[5][6]. As the addition of NO_2^+ to activated arenes (Eq. 1a) is a diffusion-controlled reaction, the reactions given in Eqs. 1b and 2 have different rates, whilst the reaction shown in Eq. 2 has a high activation energy due to the requirement that the linear nitronium ions NO_2^+ transform into the bent structure of the $NO_2^{\bullet}$ radicals during the electron transfer process. Radical reactions only occur if the radicals are generated in a different way. This is the case during irradiation of arenes with tetranitromethane; ET then takes place in excited charge-transfer complexes[7][8].

$$[C(NO_2)_4, ArH\ ]^* \rightarrow ArH^{+\bullet} + NO_2^{\bullet} + {}^{-}C(NO_2)_3 \qquad (3)$$

$Ar^{+\bullet}$ and $NO_2^{\bullet}$ might also be formed during nitration of reactive aromatic systems with dilute nitric acid. In such systems, catalysis by nitrous acid (NAC) plays an important role[3][9]. Ridd and coworkers suggest that NAC involves an electron transfer between nitrosonium cations NO^+ and arenes (Eq. 4a)[10]. NO^+ is regenerated by the reaction given in Eq. 4b to give $NO_2^{\bullet}$.

$$\begin{array}{ll} \text{NAC: } ArH + NO^+ \rightarrow ArH^{+\bullet} + NO^{\bullet} & (4a) \\ \qquad (NO^{\bullet} + NO_2^+ \rightarrow NO^+ + NO_2^{\bullet}) & (4b) \end{array}$$

Eq. 4b is enclosed in parentheses as it shows only the stoichiometry of the reaction. It does not involve free nitronium cations NO_2^+ but a more complex and, as yet, unidentified route. Under these conditions, the rate of formation of NO_2^+ is too small to allow the occurrence of the reaction given in Eq. 1a. The formation of nitration products via the reaction given in Eq. 1b has been shown by ^{15}N-CIDNP to occur during the nitration of *p*-substituted phenols, polymethylbenzenes, arylamines and naphthalenes[5].

If two different nitration products are formed during the nitration of phenolic compounds with nitric acid, their ratio depends on the concentration of sodium nitrite added to the reaction mixture. This indicates the presence of a second reaction catalysed by nitrous acid, which is a nitrosation followed by oxidation (NOX)[11].

$$\begin{array}{ll} \text{NOX: } ArH + HNO_2 \rightarrow ArNO + H_2O & (5a) \\ \qquad ArNO + HNO_3 \rightarrow ArNO_2 + HNO_2 & (5b) \end{array}$$

Aromatic *C*-nitrosation (Eq. 5a) is often described as an electrophilic substitution reaction with nitrosonium ions NO^+ as the electrophile (Eq. 6a)[11]. It has been suggested that the reaction might have a radical mechanism (Eq. 6b), analogous to the nitration reaction (Eq. 1b).

$$\begin{array}{llll} ArH + NO^+ & \rightarrow ArH^+{-}NO & \rightarrow Ar{-}NO + H^+ & (6a) \\ ArH^{+\bullet} + NO^{\bullet} & \rightarrow ArH^+{-}NO & \rightarrow Ar{-}NO + H^+ & (6b) \\ & & \quad \mathbf{3} & \end{array}$$

3: *p*-Nitrosophenol.

1434–193X/98/0505–0913 $ 17.50+.50/0

The purpose of this work is to investigate the reaction mechanism of the nitration reaction of **1** using different nitration agents. First, ^{15}N-CIDNP results obtained during the photonitration of **1** with ^{15}N-labelled tetranitromethane will be presented. The appearance of free radicals during the photoreaction of tetranitromethane with activated arenes has already been shown using time-resolved spectroscopy and ESR[7][12], and has been postulated to occur during the photoreaction with **1**[13] The second reaction is the nitration of **1** with dilute nitric acid, which will be studied by ^{15}N-CIDNP in water and different organic solvents under the conditions customary in synthetic work. The radical character of the reaction (NAC, Eqs. 4) has been postulated using kinetic arguments[14][15] but has not been proven by spectroscopic techniques. There is no doubt, however, that an electrophilic substitution reaction takes place during the nitration of **1** with a mixture of concentrated nitric and sulfuric acid (Eq. 1a) in the presence of effective scavengers for nitrous acid[16]. During the reaction of **1** with nitric acid in the presence of sodium nitrite, **2b** is formed in high yield, which has been explained by NOX (Eqs. 5a,b)[14]. To provide evidence for this ^{15}N-CIDNP studies have also been performed during the reaction of **1** with sodium nitrite.

The magnitude of the ^{15}N-CIDNP effects, taking into account enhancement factors which are determined experimentally, will be discussed and compared with calculations basing on Pedersen's formulation of the radical-pair theory[17]. This procedure, which allows the importance of the radical reactions to be determined, has already been applied with success to the nitration of 1,2-dimethoxybenzene, anisole and mesitylene[18].

Results and Discussion

Photonitration of 1 with Tetranitromethane and Nitration with Nitric Acid in Acetonitrile: ^{15}N-NMR spectra taken before, during and after irradiation of **1** in ^{15}N-labelled tetranitromethane and acetonitrile are given in Figures 1a−c. Irradiation was carried out with the visible light (λ = 488, 514 nm) of an argon ion laser in the modified probe head of a ^{15}N-NMR spectrometer. The ^{15}N-NMR signals observed after irradiation are due to $HC(^{15}NO_2)_3$ and the nitration products **2a** and **2b** (see Eqs. 1b, 3), which are formed with a ratio of 1.1. This is similar to the value of 1.3 found by Seltzer and coworkers for cyclohexane[13]. During irradiation the ^{15}N-NMR signals due to **2a** and **2b** show emission, and the signals of $HC(^{15}NO_2)_3$ and $C(^{15}NO_2)_4$ do not show CIDNP. The assignment of the signals and further details are given in Table 1.

After treatment of **1** (0.5 M) with ^{15}N-labelled nitric acid (1.25 M) in acetonitrile at room temp., **2a** and **2b** are again formed with a ratio of 1.1. If the reaction is carried out in the probe head of the ^{15}N-NMR spectrometer, the signals show emission for about 1/2 h (see Figure 2a). After 2 h, the reaction is completed, and the intensities of the ^{15}N-NMR signals of **2a** and **2b** correspond to the yields of the products (see Figure 2b); the assignments and the intensities of the signals are given in Table 1. The longitudinal relaxation times T_1 of the ^{15}N nuclei in **2a** and **2b** which have been measured after completion of the reaction are 180 s and 120 s. For a quantitative analysis the reaction is too fast. In further experiments lower concentrations of the starting compounds have been used in order to retard the reaction rate (see Table 1). The time dependence of the emission signals during the reaction of **1** (0.2 M) with ^{15}N-enriched nitric acid (0.5 M) is shown in Table 2.

The nature of the nitration products, the yields and the ^{15}N-CIDNP effects observed, are the same in both systems, indicating an identical formation path for the products. It is concluded from the ^{15}N-CIDNP effects that they are built up in radical pairs which are formed by encounters of the independently generated radicals $\mathbf{1}^{+\bullet}$ and $^{15}NO_2^{\bullet}$ ("F"- case, Eq. 7).

$$\mathbf{1}^{+\bullet} + {}^{15}NO_2^{\bullet} \rightarrow [\mathbf{1}^{+\bullet}, {}^{15}NO_2^{\bullet}]^F \rightarrow \mathbf{2a,b} + H^+ \qquad (7)$$

The radicals are formed by the reactions shown in Eqs. 3 and 4. Similar CIDNP effects have been observed during the nitration of a number of activated aromatic compounds with nitric acid, and these have been explained in an analogous fashion[5][18]. Eq. 7 describes only one possibility for product formation during the photoreaction of tetranitromethane with phenolic compounds. The photo-^{15}N-CIDNP effects might therefore be generated by, at least in part, a different radical reaction. They might be built up in geminate pairs formed by the decomposition of excited charge-transfer complexes from triplet states ("T" case). Free radicals might also be formed during the decomposition of unstable intermediates such as the nitro-trinitromethyl adducts of **1** or trinitromethyl-substituted phenols, which are formed as primary products during the irradiation of tetranitromethane with phenolic derivatives[6]. Under our conditions, however, we did not detect any ^{15}N-NMR or ^{15}N-CIDNP signals which might be due to such compounds.

The importance of non-radical nitration reactions will be discussed by comparing experimentally determined enhancement factors (E) with calculated ones (E_{calc}), since only the radical reactions lead to ^{15}N-CIDNP. E values, which have been determined from the data given in the Tables 1 and 2 by applying Eqs. 9 and 10, E_{calc} values with $g(\mathbf{1}^{+\bullet}) = 2.00291$[19], and the parameters used for calculating enhancement factors of ^{15}N-CIDNP effects in the nitration products of 1,2-dimethoxybenzene and anisole[18] are listed in Table 3. The radical cation $\mathbf{1}^{+\bullet}$ might exist in its unprotonated form $PhO^{\bullet}$, and so further calculations have therefore been performed using $g(PhO^{\bullet}) = 2.00461$[19]. E values lie between −500 and −1000 and E_{calc} values between −1000 and −1100. Within the limits of the experimental and theoretical accuracy the values are comparable, showing that there is no reason to assume that non-radical reactions are of major importance during the photochemical nitration of **1** with tetranitromethane, or during the nitration of **1** with nitric acid. It cannot be determined from the ^{15}N-CIDNP experiments whether radical cations $\mathbf{1}^{+\bullet}$ or phenoxyl radicals $PhO^{\bullet}$ are involved in the nitration of **1** .

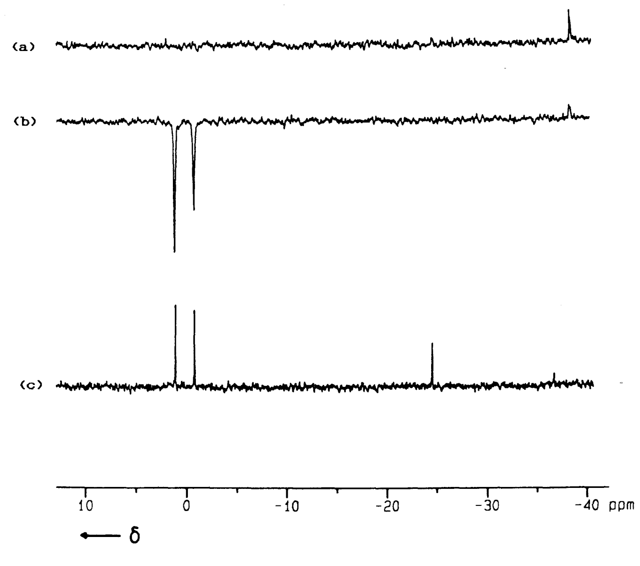
Reactions of 1 with Nitric Acid in Water and Acetic Acid: The nitration of **1** with diluted nitric acid was first de-

Table 1. ^{15}N-CIDNP during nitration of **1** with ^{15}N-enriched systems (ACN: acetonitrile)

System	Solvent	^{15}N Signals[a]		I_{max}	I_{max}[b]	I_o	t_E[c]
$C(NO_2)_4$ (0.18 M)	ACN/[D$_3$]ACN	−38.6 [$C(^{15}NO_2)_4$]					
(Figure 1)[d]	= 50:1	−24.8 [$HC(^{15}NO_2)_3$]					
		−0.2 (**2b**)	*E*	−19.0	[e]	13.5	76
		1.8 (**2a**)	*E*	−27.7	[e]	14.5	7
HNO_3 (1.25 M)	ACN/H_2O + D_2O	−5.6 ($H^{15}NO_3$)					
(Figure 2)[f]	= 9:1	0.8 (**2b**)	*E*	−1200	6	13.5	30
		2.3 (**2a**)	*E*	−1800	6	15.0	30
HNO_3 (0.5 M)	ACN/H_2O+D_2O	0.8 (**2b**)	*E*	−330	25	4.5	120
(Table 2)[g]	= 9:1	2.3 (**2a**)	*E*	−390	25	5.0	120
HNO_3 (1.7 M)	H_2O/D_2O	0.7 (**2b**)	*E*	−35	120	–	240[h]
(Figure 3a)[f]	= 20:1	1.8 (**2a**)	*E*	−50	120	–	240[h]
		4.3 ($H^{15}NO_3$)					
HNO_3 (1.25 M)[f]	AcOH/D_2O	−0.6 (**2b**)	*A*	5	[i]	6	3
	= 9:1	0.9 (**2a**)	*A*	6	[i]	5	3
HNO_3 (0.5 M)[g]	AcOH/D_2O	−0.6 (**2b**)	*E*	−677	2	15	5
	= 9:1	0.9 (**2a**)	*E*	−1000	2	12	5
$NaNO_2$ (0.3 M)	H_2O+D_2O/H_2SO_4	0.8 (**2b**)	*E*	−17	3	–	6[j]
(Figure 3b)[g]	= 9:1	1.7 (**2a**)	*E*	−25	3	–	6[j]
		3.2 ($^{15}NO_3^-$)	*N*[k]	22	3	–	10[j]
$NaNO_2$ (0.3 M)	AcOH/D_2O	−0.6 (**2b**)	*E*	−10	3	1.2	90[l]
(Figure 4, Table 2)[g]	= 9:1	0.9 (**2a**)	*E*	−15	3	0.7	90[l]
		3.2 ($^{15}NO_3^-$)	*N*[k]	20	3	5.0	40[l]
		60 (**3**)	*N*				

[a] δ values against $Ph^{15}NO_2$, positive δ values downfield; *E*: emission, *A*: enhanced absorption, *N*: no ^{15}N-CIDNP. – [b] I_{max}: maximal intensity of *E* or *A* (signal-to-noise ratio). t_{max}: time of I_{max} after addition of ^{15}N-enriched HNO_3 or $NaNO_2$ to the solutions (min). – [c] I_o: signal intensity after reaction (signal-to-noise ratio), t_E: duration of the ^{15}N-CIDNP effects (min). – [d] [PhOH] = 0.64 M; *T* = 298 K. Irradiation with the unfiltered light of a LEXEL 95 argon ion laser within the probe head of the ^{15}N-NMR spectrometer, 30 pulses with 13°, delay time 3 s, after irradiation 501 pulses. – [e] ^{15}N-CIDNP intensities are constant during the irradiation. – [f] *T* = 300 K, single 90° pulses, [PhOH] = 0.5 M. – [g] *T* = 300 K, single 90° pulses, [PhOH] = 0.2 M. – [h] Besides $H^{15}NO_3$, ^{15}N-NMR signals could not be detected after reaction (**2a** and **2b** are not soluble in diluted HNO_3). – [i] The reaction was completed before taking the first spectrum. – [j] ^{15}N-NMR signals of **2a** and **2b** could not be detected after reaction (**2a** and **2b** are not soluble in diluted H_2SO_4). – [k] The ^{15}N-NMR signal might exhibit a small *A*-type CIDNP effect. – [l] I_o values taken from spectra taken after reaction, 64 pulses with 90°, delay time 10 min.

Figure 1. ^{15}N-NMR spectra of **1** and ^{15}N-enriched $C(NO_2)_4$ in ACN/[D$_3$]ACN (ACN: acetonitrile), (a) before (30 scans), (b) during (30 scans) and (c) after irradiation (501 scans) with the unfiltered light of an argon ion laser (pulse angle 13°, delay time 3 s)



scribed by A. W. Hofmann in 1850[20]. If the reaction of **1** (0.5 M) with ^{15}N-enriched nitric acid (1.7 M) is performed within the probe head of the ^{15}N-NMR spectrometer two emission signals are observed (see Figure 3a), which disappear after about 4 h. The comparison with the ^{15}N-CIDNP effects observed in acetonitrile (Figure 2a) shows that the signals are due to **2a** and **2b**. As **2a** and **2b** are not soluble in diluted nitric acid, ^{15}N-NMR signals could not be observed after the reaction, and a quantitative analysis of the ^{15}N-CIDNP effects was not possible. Nevertheless, the radical character of the nitration reaction which was first postulated by Ross and coworkers[14] is evident even in water.

The formation of **2a** and **2b** is also described with acetic acid as the solvent[21], and ^{15}N-CIDNP effects have also been observed. During the reaction of ^{15}N-enriched nitric acid (1.25 M) with **1** (0.5 M) , the reaction is completed before taking the first spectrum, and the signals of **2a** and **2b** show enhanced absorption. Using a solution of ^{15}N-enriched nitric acid (0.5 M) and of **1** (0.2 M), the reaction is completed within 5 min, and the ^{15}N-NMR signals of **2a** and **2b** appear in emission, as was the case with acetonitrile and water. The results are compiled in Table 1. The reactions are too fast to allow a quantitative analysis. ^{15}N-NMR signals of **2a** and **2b** can be detected after the reaction which allows the determination of the T_1 values shown in Table 3.

The emission, as well as the enhanced absorption, observed in **2a** and **2b** can be explained as above (Eq. 7). The reaction of independently generated radicals $1^{+\bullet}$ and $^{15}NO_2^{\bullet}$ only leads to emission if the reaction is run in magnetic fields which are large compared with $a_N(NO_2^{\bullet})$. At

Table 2. ^{15}N-NMR intensities I[a] of **2a,b** and $^{15}NO_3^-$ (a) during reaction of **1** (0.2 M) with ^{15}N-enriched HNO_3 (0.5 M) in ACN at 300 K, (b) during reaction of **1** (0.2 M) with ^{15}N-enriched $NaNO_2$ (0.3 M) in AcOH at 300 K

(a)														
t[b]	5	15	25	35	45	55	65	75	85	95	105	115	125	600
I(**2a**)	−25	−280	−390	−157	−125	−63	−33	−24	−16	−10	−4	−2	–	5.0
I(**2b**)	−24	−190	−330	−127	−100	−45	−25	−19	−11	−6	−2	−1	–	4.5

(b)														
t[b]	3	6	9	12	15	18	24	36	48	60	72	84	96	300
I(**2a**)	−15	−58	−42	−24	−24	−18	−17	−12	−12	−6	−5	−2	–	0.7[c]
I(**2b**)	−10	−27	−22	−17	−14	−11	−10	−7	−5	−4	−3	−1	–	1.2[c]
$I(NO_3^-)$	20	52	27	12	11	9	6	6	5	5	5	5	5	5

[a] Determined from the signal-to-noise ratio using single 90° pulses. – [b] t: time after mixing the reactants and putting the tube into the probe head of the spectrometer (min). – [c] Values from spectra taken after the reaction, 64 pulses with 90°, delay time 10 min.

low magnetic fields the recombination of free radicals should give enhanced absorption, as is observed[18].

Figure 2. ^{15}N-NMR spectra during reaction of **1** with ^{15}N-enriched HNO_3 in ACN at 300 K (a) 6 min, (b) 30 min after mixing the reactants (single 90° pulses)

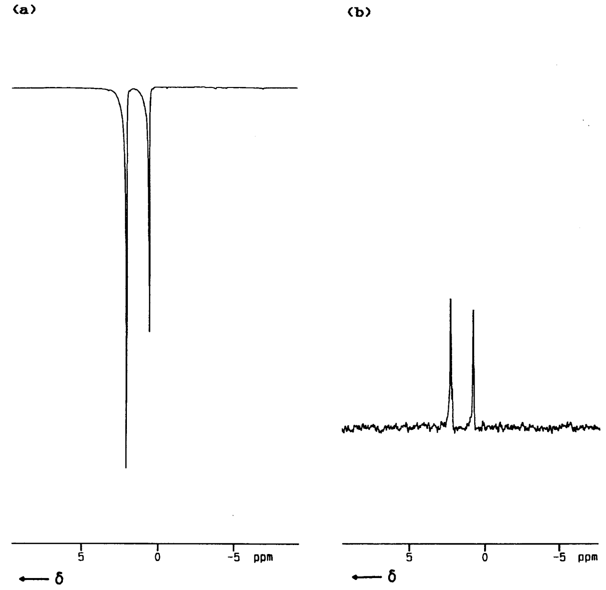


Figure 3. ^{15}N-NMR spectra during reaction of **1** (a) with ^{15}N-enriched HNO_3 in H_2O/D_2O 120 min after mixing the reactants, (b) with ^{15}N-enriched $NaNO_2$ in diluted H_2SO_4 3 min after mixing the reactants (single 90° pulses)

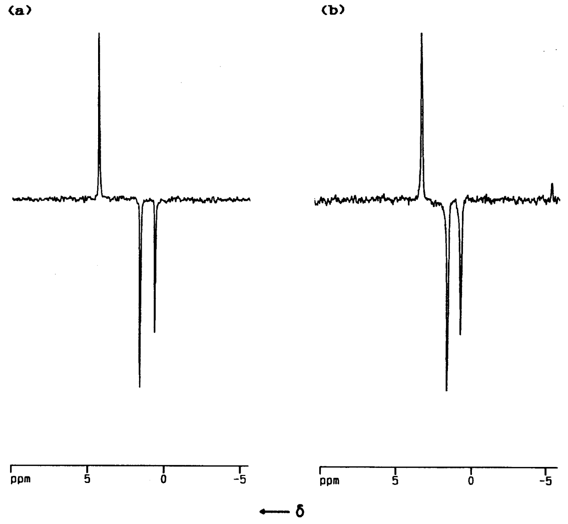


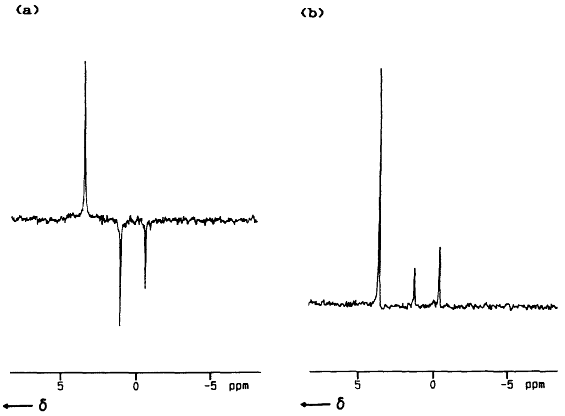
Table 3. Experimental enhancement factors E of ^{15}N-CIDNP effects in **2a** and **2b** and calculated ones E_{calc}[a].

Compound, solvent	ESR[19] and NMR parameters	Enhancement factors
2a in ACN	T_1 = 180 s	$E = -500$[b] $E = -750$[c]
2b in ACN	T_1 = 120 s	$E = -550$[b] $E = -980$[c]
2a,b in ACN	$g(\mathbf{1}^{+\bullet}) = 2.00291$ $g(PhO^\bullet) = 2.00461$	$E_{calc} = -1025$ $E_{calc} = -1092$
2a in AcOH	T_1 = 90 s	$E = -1180$[d]
2b in AcOH	T_1 = 54 s	$E = -650$[d]
2a,b in AcOH	$g(\mathbf{1}^{+\bullet}) = 2.00291$ $g(PhO^\bullet) = 2.00461$	$E_{calc} = -1260$ $E_{calc} = -1256$

[a] Calculated with Pedersen's treatment of the radical-pair theory[17][18]. – [b] During irradiation of ^{15}N-enriched $C(NO_2)_4$ with **1**. – [c] During reaction of ^{15}N-enriched HNO_3 with **1**. – [d] During reaction of ^{15}N-enriched $NaNO_2$ with **1**.

Reactions of 1 with Nitrous Acid in Water and Acetic Acid: The nitrosation of **1** was first studied by A. Baeyer and H. Caro in 1874[23]. By treating an aqueous solution of **1** and $NaNO_2$ or KNO_2 with sulphuric acid or acetic acid, *p*-nitrosophenol (**3**) is formed as the main product[22][23] (Eq. 5a). During the reaction of **1** with ^{15}N-enriched $NaNO_2$ in diluted sulfuric acid and acetic acid in the probe head of the NMR spectrometer, two emission signals and one absorption signal are observed (see Figures 3b, 4a and Table 1). After the reaction in dilute sulfuric acid, ^{15}N-NMR signals of the reaction products could not be observed because of their low solubility in water. This was not the case with acetic acid as the solvent; Figure 4b shows a ^{15}N-NMR spectrum of the products taken in acetic acid 120 min after mixing the reactants. It follows that the emission signals are due to **2a** and **2b** which are formed as side products of the reaction. The effects are identical with those observed during the reaction of **1** with nitric acid and explained in the same manner. $NO_2^\bullet$ and NO_3^- are formed by disproportionation[24].

Figure 4. ^{15}N-NMR spectra (a) during reaction of **1** with ^{15}N-enriched $NaNO_2$ in AcOH with a single 90° puls (b) 120 min after completion of the reaction (64 90° pulses , delay time 10 min)



$$2\ HNO_2 \rightleftharpoons NO^\bullet + NO_2^\bullet + H_2O \qquad (8a)$$
$$2\ NO_2^\bullet + H_2O \rightleftharpoons HNO_2 + H^+ + NO_3^- \qquad (8b)$$

The reaction is slow enough to allow the determination of ^{15}N-CIDNP intensities and enhancement factors E and E_{calc} (see Tables 2 and 3). In the case of **2a** , the results agree well with those found during the reaction of **1** with nitric acid in acetonitrile. The E values of **2b** are somewhat lower than those observed for **2a,** which is explained by a non-radical formation of **2b** in part via NOX (Eqs. 5a,b), and this has been postulated to occur during the nitration of **1** with nitric acid in the presence of nitrous acid[14].

The absorption signal observed at $\delta = 3.2$ is assigned to $^{15}NO_3^-$ or $H^{15}NO_3$[25] (Eq. 8b). The intensity is higher as expected, indicating a slightly enhanced absorption. This might be a polarisation of "e"-type built up in $^{15}NO_2^\bullet$ during the reaction shown in Eq. 7[26], which is transferred to $^{15}NO_3^-$ by Eq. 8b. The ^{15}N-NMR signal of the nitrosation product (**3**), which is the main product, does not show a ^{15}N-CIDNP effect which might be formed during the recombination reaction of $^{15}NO^\bullet$ with $1^{+\bullet}$ (Eq. 6b).

Both radicals are present as is indicated by the appearance of ^{15}N-CIDNP in **2a** and **2b**. The absense of ^{15}N-CIDNP effects does not prove the non-radical mechanism of the nitrosation reaction. The low g value of $NO^\bullet$ (1.95[19]) makes it difficult or impossible to observe CIDNP. The transversal relaxation time T_2 in solution is not known. A low value of T_2 has to be expected because of the orbitally degenerated ground state of the radicals $NO^\bullet$. This would also diminish the magnitude of the effect. There are further chemical reasons which make it probable that a radical *C*-nitrosation is the main reaction, and that an electrophilic aromatic substitution reaction (Eq. 6a) only plays a minor role, if any. *C*-nitrosation only happens with aromatic compounds that are more reactive than toluene[11]. These are the same systems which are nitrated via the radical pathway NAC (Eqs. 4). Furthermore, it has been estimated that NO^+ is less reactive than NO_2^+ by a factor of 10^{14} [28], which makes an electrophilic substitution (Eq. 6a) unlikely if there is any other reaction possibility.

Conclusion

^{15}N-CIDNP effects have been observed in the nitration products of **1** during three different nitration procedures, a photonitration with tetranitromethane and the reactions with nitric and nitrous acid. The effects are identical indicating a common reaction step, which is the recombination of the radicals $NO_2^\bullet$ with radical cations $\mathbf{1}^{+\bullet}$ or phenoxyl radicals $PhO^\bullet$ (Eq. 7), for the product formation in all the three systems, one of the rare examples of a radical cation-radical reaction[27]. In the case of the photochemical reaction, the radicals are generated by electron transfer in the photoactivated state of a charge-transfer complex of tetranitromethane (Eq. 3). They are also formed by nitrous acid catalysis and decomposition during the reaction with nitric and nitrous acid (NAC, Eqs. 4a,b, 8b).

Applying the nitrous acid system, **2b** is formed in part via a non-radical reaction, which is a nitrosation followed by oxidation (NOX, Eqs. 5a,b). The presence of the radicals $NO^\bullet$ and $\mathbf{1}^{+\bullet}$ make it probable that the formation of **3** occurs via recombination and deprotonation (Eq. 6b). It might be concluded that not only the nitration, but also the *C*-nitrosation of aromatic compounds with distinct electron-donor properties, is a radical reaction in general.

This work was supported by the *Fonds der Chemischen Industrie.* We thank *Radiant Dyes*, Wermelskirchen, Germany, for giving us the possibility for using the argon ion laser.

Experimental Section

Photochemical ^{15}N-CIDNP Experiments: The photochemical experiments were performed within a modified ^{15}N-NMR probe head of a Bruker DPX-300 NMR spectrometer equipped with a light conductor which was connected to a LEXEL 95 Ar-Ion Laser (Polytec Inc.) The degassed reaction mixtures were irradiated at room temp. with the unfiltered light of the laser [λ = 514 nm (2.9 W), λ = 488 nm (2.4 W)]. The spectra were taken with 30 scans of 13^0 pulses with a delay time of 3 s. After an irradiation time t_E, spectra were taken with 501 scans. ^{15}N-chemical shifts are reported in δ values downfield relative to the standard Ph-$^{15}NO_2$, ^{1}H- and ^{13}C-NMR data relative to TMS. Raman spectra were recorded on a T 64000 (ISA) with an argon laser at λ = 514.4 nm (Spectra Physics). Enhancement factors E were determined by using Eq. 9[18][28].

$$E = I_{max} t_E / I_o T_1 \qquad (9)$$

I_{max}, the intensity of the CIDNP signal, and I_o, the intensity after irradiation, were taken from the spectra under consideration of the different scan numbers. An estimated filling factor of 2 was taken into account. ^{15}N-nuclear longitudinal relaxation times T_1 were determined by applying $\pi-\pi/2$ pulse sequences. For getting appropriate signal-to-noise ratios, delay times have been applied which are much shorter than the T_1 values[29]. **2a**, **2b** and $HC(NO_2)_3$ were identified by using ^{1}H-, ^{13}C-, ^{14}N- and ^{15}N-NMR data. The product ratio of **2a** and **2b** (1.1) was taken from ^{1}H-NMR spectra and proved by GC analysis [GC DANI Mod. 8521-A(25 m CP-SIL-5CB)].

Preparation of Tetranitromethane-^{15}N : The compound was synthesized as described[30]. $NaNO_3$ with 10 atom% ^{15}N was used (Isotec Inc.). − ^{15}N NMR (CD_3CN): $\delta = -38.6$ (s). − ^{13}C NMR (CD_3CN): $\delta = 115.4$ (q). − Raman: $\tilde{\nu} = 1615\ cm^{-1}$, 1649 ($\nu_a$ NO_2); 1341, 1247 (ν_s NO_2); 360, 408, 417, 608 (δ NO_2).

Thermal ^{15}N-CIDNP Experiments: After putting the reactants into the 10-mm NMR tubes, they were quickly transferred into the probe head of the ^{15}N-NMR spectrometer and locked within 2 min (internal lock: D_2O). ^{15}N-NMR spectra were then taken every 3−12 min using single pulses with a pulse angle of 90° until the reactions were completed. ^{15}N-NMR relaxation times T_1 were then determined applying $\pi-\pi/2$ pulse sequences. The repetition times were long enough to avoid saturation. Shorter pulses have also been applied. They give identical results, but have not been used for the quantitative measurements, as the signal-to-noise ratio of I_{max} and I_o is somewhat smaller. The identification of **2a**, **2b**, **3** and NO_3^- was performed by comparing ^{13}C-, ^{14}N- and ^{15}N-NMR data with those of authentic material and the literature[25]. Product ratios were taken from ^{15}N-NMR and ^{13}C-NMR spectra. The nitric acid used was 9.4 M in H_2O and labelled with 60.3 atom% ^{15}N (Isotec Inc.). $NaNO_2$ was labelled with 99.3 atom% ^{15}N (Isotec Inc.). All the compounds and solvents were commercial and used without further purification. E was determined using Eq. 10[18].

$$E = \Sigma\ I_i\Delta\ t(i,i+1)/I_oT_1 \qquad (10)$$

I_i is the intensity of the ith measurement, $\Delta t(i,i+1)$ the time interval between the ith and the (i+1)th measurement. The summation was carried out as long as the CIDNP effects could be observed. For improving the signal-to-noise ratio of I_o, several 90° pulses with a delay time of 10 min were used in some cases.

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[1] G. A. Olah, R. Malhotra, S. C. Narang, *Nitration*, Verlag Chemie, New York **1989**; K. Schofield, *Aromatic Nitration*, Cambridge University Press, Cambridge **1980**.

[2] T. M. Bockman, J. K. Kochi, *J. Phys. Org. Chem.* **1994**, *7*, 325−351; L. Eberson, M. P. Hartshorn, F. Radner, *Advances in Carbocation Chemistry*, Ed. J. M. Coxon, JAI Press, London **1995**, vol. 2, pp 207−263.

[3] C. A. Bunton, E. D. Hughes, G. J. Minkoff , R. I. Reed, *Nature (London)* **1946**, *158*, 514−515; E. D. Hughes, C. K. Ingold, R. I. Reed, *J. Chem. Soc.* **1950**, 2400−2440; C. A. Bunton, E. D. Hughes, C. K. Ingold, D. I. H. Jacobs, M. H. Jones, G. J. Minkoff, R. I. Reed, *J. Chem. Soc.* **1950**, 2628−2656.

[4] J. Kenner, *Nature (London)* **1945**, *156*, 369−370; C. L. Perrin, *J. Am. Chem. Soc.* **1977**, *99*, 5516−5518.

[5] J. H. Ridd, *Chem. Soc. Rev.* **1991**, *20*, 149−165.

[6] L. Eberson, F. Radner, *Acta Chem. Scand. B,* **1984**, *38*, 861−870; T. Lund, L. Eberson, *J. Chem. Soc., Perkin Trans. 2,* **1997**, 1435−1443.

[7] S. Sankararaman, W. A. Haney, J. K. Kochi, *J. Am. Chem. Soc.* **1987**, *109*, 5235−5249.

[8] L. Eberson, M. P. Hartshorn, F. Radner, J. O. Svensson, *Acta Chem. Scand.* **1996**, *50*, 885−898; C. P. Butts, L. Eberson, M. Hartshorn, O. Persson, *Acta Chem. Scand.* **1997**, *51*, 718−732; C. P. Butts, L. Eberson, M. P. Hartshorn, O. Persson, R. S. Thompson, W. T. Robinson, *Acta Chem. Scand.* **1997**, *51*, 1066−1077.

[9] H. Martinsen, *Z. Phys. Chem.* **1904**, *50*, 385−435.

[10] J. C. Giffney, J. H. Ridd, *J. Chem. Soc., Perkin Trans. 2,* **1979**, 618−623.

[11] D. L. H. Williams, *Nitrosation*, Cambridge University Press, Cambridge **1988** ; B. C. Challis, A. J. Lawson, *J. Chem. Soc. (B)* **1971**, 770−775; B. C. Challis, R. J. Higgins, A. J. Lawson, *J. Chem. Soc., Perkin Trans. 2,* **1972**, 1831−1836.

[12] L. Eberson, M. P. Hartshorn, O. Persson, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2268−2269; L. Eberson, O. Persson, F. Radner, M. P. Hartshorn, *Res. Chem. Intermed.* **1996**, *22*, 799−820.

[13] S. Seltzer, E. Lam, L. Packer, *J. Am. Chem. Soc.* **1982**, *104*, 6470−6471.

[14] D. S. Ross, G. P. Hum , W. G. Blucher, *J. Chem. Soc., Chem. Comm.* **1980**, 532−534.

[15] F. Radner, A. Wall, M. Loncar, *Acta Chem. Scand.* **1990**, *44*, 152−157.

[16] R. G. Coombes, J. G. Golding , P. Hadjigeourgiou, *J. Chem. Soc., Perkin Trans. 2,* **1979**, 1451−1459.

[17] J. B. Pedersen, *J. Chem. Phys.* **1977**, *67*, 4079−4102.

[18] M. Lehnig, *J. Chem. Soc., Perkin Trans. 2,* **1996**, 1943−1948; M. Lehnig, *Acta Chem. Scand.* **1997**, *51*, 211−213; M. Lehnig, *Chem. Phys.* **1975**, *8*, 419−424; **1981**, *54*, 323−329.

[19] Landolt-Börnstein, Neue Serie Bd. 9, 17, *Magnetische Eigenschaften freier Radikale*, Ed. H. Fischer, K.-H. Hellwege, Springer-Verlag Berlin, Heidelberg, New York, **1987**.

[20] A. W. Hofmann, *Ann. Chem. Pharm.* **1850**, *LXXV*, 356−368.

[21] F. Arnall, *J. Chem. Soc.* **1924**, 811−816.

[22] J. L. Bridge, *Liebigs Ann. Chem.* **1893**, *277*, 79−104.

[23] A. Baeyer, H. Caro, *Ber. Dtsch. Chem. Ges.* **1874**, *7*, 963−968.

[24] B. D. Beake, J. Constantine, R. B. Moodie, *J. Chem. Soc., Perkin Trans. 2* **1992**, 1653−1654.

[25] M. Witanowski, L. Stefaniak, G. A. Webb, *Ann. Rep. NMR Spectrosc.* **1993**, *25*, 1, and references cited therein.

[26] R. Kaptein, *Chem. Comm.* **1971**, 732−733.

[27] M. Schmittel, A.Burghart, *Angew. Chem.* **1997**, *109*, 2658−2699.

[28] M. Lehnig, H. Fischer, *Z. Naturforsch., Teil A,* **1970**, *25*, 1963−1969; **1972**, *27*, 1300−1307.

[29] R. R. Ernst, W. A. Anderson, *Rev. Sci. Instrum.* **1966**, *37*, 93.

[30] W. Skawinski, J. Flisak, A. C. Chung, F. Jordan, R. Mendelsohn, *J. Labelled Compds.* **1990**, *28*, 1179−1183.

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