

A Practical Scale for Measuring the Acidity of Media for the Generation of Radical Cations for EPR Spectroscopy

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1,4,5,8-Tetramethylnaphthalene (**1**) undergoes a facile rearrangement first to 1,3,5,8-tetramethylnaphthalene (**3**) and then to other tetramethylnaphthalenes upon treatment with Brønsted and/or Lewis acids, but is stable toward rearrangement at the radical cation level ($1^{\cdot+}$). By measuring the rate constant of the rearrangement of **1**→**3**, a practical scale of the Brønsted/Lewis acidity of certain oxidant–solvent combinations commonly used to generate radical cations for EPR spectroscopy can be established. The results show that the reactivity falls in the order $\text{AlCl}_3 \gg \text{CF}_3\text{SO}_3\text{H} > \text{H}_2\text{SO}_4 > \text{H}_3\text{O}^+ \gg \text{CF}_3\text{COOH} \approx \text{SbCl}_5$. Antimony pentachloride does not catalyze the rearrangement but acts as a chlorinating agent.

A large variety of methods exists for the one-electron oxidation of neutral molecules in order to prepare solutions of the corresponding radical cations persistent enough for EPR spectroscopic study.^{1–3} One source of unwanted reactivity is the presence of nucleophilic species, which is often suppressed by the addition of a Brønsted and/or Lewis acid to the medium. Such additives decrease the nucleophilicity by protonation of and/or association with nucleophilic sites. Sulfuric acid, oleum, aluminium chloride in various inert solvents, Tl^{III} trifluoroacetate–trifluoroacetic acid, Hg^{II} trifluoroacetate–trifluoroacetic acid and antimony trichloride–antimony pentachloride are examples of media which have been used frequently in the EPR spectroscopic practice. However, acidity may not be the only parameter by which radical cation persistence can be influenced; 1,1,1,3,3,3-hexafluoro-2-propanol ($\text{p}K=9.3$) was recently shown to be vastly superior to trifluoroacetic acid ($\text{p}K=0.3$) in prolonging the half-lives of radical cations.⁴

The main disadvantage of adding an acid as stabilizer is the risk of causing undesirable acid-catalyzed transformations of the substrate prior to oxidation. Such complications are known, for example when aluminium chloride is present, and can be difficult to discern on the basis of EPR spectroscopy alone when choices of species of many different hfs constants and multiplicities are involved. It would therefore be desirable to classify the oxidative media used for radical cation EPR spectroscopy according to their Brønsted/Lewis acidity. In what follows we devise a method for such classification based

on the acid-induced rearrangement of 1,4,5,8-tetramethylnaphthalene to 1,3,5,7-tetramethylnaphthalene. The practical range of the scale obtained covers almost seven powers of ten of reactivity.

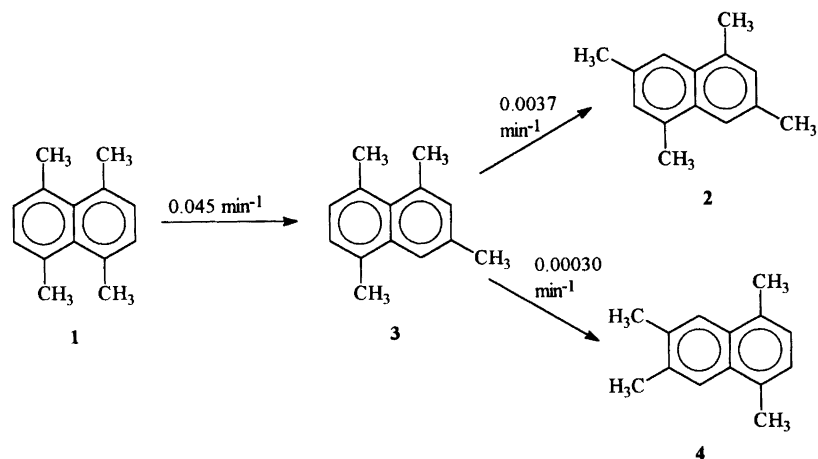
Results

Background. When 1,4,5,8-tetramethylnaphthalene (**1**) was oxidized by 2,3-dichloro-4,5-dicyanobenzoquinone (DDQ) in trifluoroacetic acid (TFA) at room temperature or was photolyzed in the presence of tetranitromethane in dichloromethane–TFA (5%) at -20°C , a well resolved EPR spectrum of $1^{\cdot+}$ was obtained.⁵ When instead the oxidation was performed in TFA–trifluoromethanesulfonic (triflic) acid (10% v/v $\approx 1.1 \text{ mol dm}^{-3}$)⁶ a different EPR spectrum was recorded; eventually it was traced to that of the 1,3,5,7-tetramethylnaphthalene radical cation ($2^{\cdot+}$),⁷ presumably formed by an acid-catalyzed rearrangement of **1** to **2**, followed by oxidation of **2** by triflic acid.

This rearrangement has previously been studied⁸ in neat TFA in the temperature range of 40 – 77°C , and has been shown to involve successive 1,2-methyl shifts according to Scheme 1, 1,3,5,8-tetramethylnaphthalene (**3**) being the first rearrangement product from **1**. Compound **3** is then rearranged to a mixture of **2** and 1,4,6,7-tetramethylnaphthalene (**4**), with the former predominating. The rate constants given⁸ refer to a temperature of 70°C .

The slowness of the first reaction at low temperatures suggested that this rearrangement might be used as a probe for the Brønsted and/or Lewis acid reactivity of

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Scheme 1

radical cation generating media, provided that any rearrangement of $1^{\cdot+}$ is slow in comparison to the acid-catalyzed one.

Rearrangement of 1,4,5,8-tetramethylnaphthalene (1) in dichloromethane-TFA (1:1) with 0.5% triflic acid added. The $1 \rightarrow 3 \rightarrow 2 + 4$ rearrangement of Scheme 1 was monitored with time by GLC of samples withdrawn at suitable intervals from a solution of 1 (58 mmol dm^{-3}) in dichloromethane-TFA (1:1 v/v) with 0.5% triflic acid present. The kinetic data, shown in Fig. 1, demonstrate that 1 rearranges quickly in this medium, $k_{\text{rearr}} = 0.42(2) \text{ min}^{-1}$. As expected, compound 3 is formed with the

same rate constant, $0.39(3) \text{ min}^{-1}$ and then further rearranges with a rate constant of $0.041(3) \text{ min}^{-1}$, forming 2 and 4 in a 90:8 ratio with rate constants $0.031(2)$ and $0.028(2) \text{ min}^{-1}$.

A scale of Brønsted-Lewis acidity for radical cation generating systems. The rate constant for the $1 \rightarrow 2$ rearrangement is an easily measured quantity and is thus a potential indicator for a practical acidity scale of importance for judging the suitability of media for radical cation generation. Table 1 lists rate constants for a number of Brønsted and Lewis acid of frequent use in the generation of radical cations, employing either dichloromethane or nitromethane as solvent, the choice of the latter dictated by its frequent use and better solvent properties toward acids than dichloromethane. In order to ascertain that no rearrangement takes place at the radical cation level, solutions of 1 were treated with one-electron oxidants (Table 2); either no rearrangement was observed or, in media containing trifluoroacetic acid, it took place at a rate similar to that obtained without any oxidant present. Thus, in cases where rearrangement takes place at a significant rate, it must be caused by the effect of the acidity of the medium upon the neutral molecule.

Three situations can be distinguished. First, the acidity of the medium is so low that essentially no rearrangement takes place (Table 1, nos. 1, 2, 7, 10 and 15, possibly also 5) during any period of time appropriate for recording an EPR spectrum. Second, rearrangement takes place with half-lives of 1 in the range of ca. 2 h to 0.5 min (Table 1, nos. 3-6, 8, 9 and 11), aluminium chloride being particularly reactive as a catalyst. Third, isomerization does not take place, but 1 undergoes substitution reactions as observed for mixtures containing SbCl_5 , a classical oxidant in the EPR spectroscopic literature but also being an active chlorinating agent (Table 1, nos. 12-14).

Both types of reactivity are combined for anhydrous FeCl_3 , admittedly not often used in the EPR spectro-

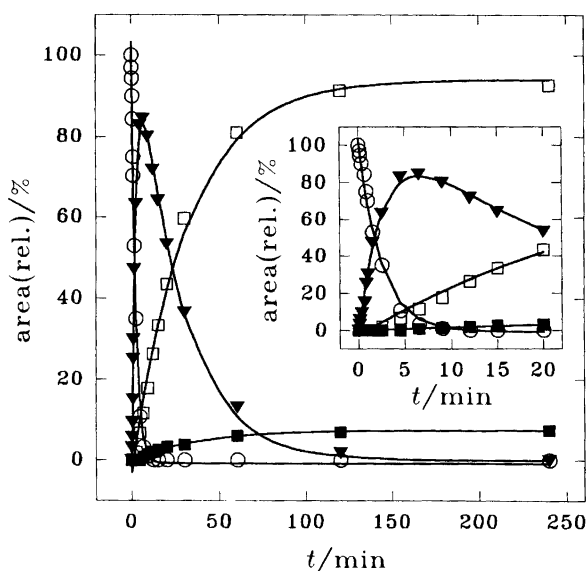


Fig. 1. Kinetics of the acid-catalyzed rearrangement of 1 (58 mmol dm^{-3}) in dichloromethane with trifluoroacetic (6.5 mol dm^{-3}) and triflic acid (57 mmol dm^{-3}) present at 22°C . Empty circles, 1; filled triangles, 3; empty squares, 2; filled squares, 4. The insert shows the events of the first 20 min. All lines represent the best fit of the data to either a three-parameter exponential (1, 2, 4) or a four-parameter double exponential (3). The corresponding rate constants are given in the text.

Table 1. Rate constant (k) for the conversion of **1** into **3** in various acidic systems at 22 °C.

No.	Acid (conc./mol dm ⁻³)	Solvent	k/min^{-1}	k_{rel}
1	Trifluoroacetic acid (8.7)	Dichloromethane	$< 10^{-6a}$	$< 2 \times 10^{-4}$
2	Trifluoroacetic acid (2.6)	Nitromethane	$< 10^{-6a}$	$< 2 \times 10^{-4}$
3	Trifluoroacetic acid (6.5) + triflic acid (0.057)	Dichloromethane	0.42	67
4	Triflic acid (0.74)	Nitromethane	0.0063	1.0
5	Sulfuric acid, 96% (0.7)	Nitromethane	3.8×10^{-4}	6×10^{-2}
6	Sulfuric acid, 96% (2.8)	Nitromethane	0.073	12
7	Perchloric acid, 70% (0.70)	Nitromethane	3.5×10^{-6b}	6×10^{-4}
8	AlCl ₃ (0.20) ^c	Nitromethane	0.13	21
9	AlCl ₃ (0.31)	Nitromethane	1.5	240
10	SbCl ₃ (0.56; 3.8)	Nitromethane	$< 10^{-6a}$	$< 2 \times 10^{-4}$
11	SbCl ₃ (3.8), AlCl ₃ (0.31)	Nitromethane	1.6	250
12	SbCl ₅ (0.31)	Dichloromethane	^d	
13	SbCl ₅ (0.030), SbCl ₃ (0.30)	Nitromethane	^e	
14	FeCl ₃ (0.3)	Nitromethane	^f	
15	BF ₃ -etherate (0.6)	Nitromethane	$< 10^{-6a}$	$< 2 \times 10^{-4}$

^a The practical limit was defined as $< 1\%$ conversion in 168 h. ^b Monochlorinated **1** (10%) was formed in 48 h. ^c At [AlCl₃] < 0.2 mol dm⁻³, rearrangement occurred but was incomplete. ^d No isomerization occurred within 6 h. Instead, fast chlorination of **1** took place with formation of mono-, di-, tri-, and tetrachlorinated tetramethylnaphthalene. With a catalytic amount of SbCl₅, the only product was monochloro-**1**. ^e Slow monochlorination of **1** occurred. ^f A complex reaction took place, involving chlorination and rearrangement (see text).

Table 2. Treatment of **1** (30 mmol dm⁻³) with various oxidizing agents at 22 °C.

Oxidant	Solvent	Rearrangement
Tris(4-bromophenyl)aminium hexachloroantimonate (8 mmol dm ⁻³)	Dichloromethane	None
Tris(4-bromophenyl)aminium hexachloroantimonate (8 mmol dm ⁻³)	Dichloromethane-trifluoroacetic acid (1:2, v/v)	Same rate as in Table 1, no. 1
Ti ^{III} trifluoroacetate	Dichloromethane-trifluoroacetic acid (1:2, v/v)	Same rate as in Table 1, no. 1

scopic practice but known as a potent electron transfer oxidant and a Lewis acid as well as a chlorinating agent,⁹ which initially chlorinated **1** in a rapid process. After 60% of the reaction had proceeded, the **1**→**3** rearrangement began to be detectable and at the same time monochlorinated **1** started to undergo rearrangement to at least two new monochlorotetramethylnaphthalenes. Compound **3** was also chlorinated and/or rearranged. After 100 min, the reaction mixture contained 17% **2**, 70% monochlorinated tetramethylnaphthalenes and 12% dichlorinated ones.

Discussion

The log k_{rel} values of Table 1 are represented in the bar diagram of Fig. 2. As expected, the strong Lewis acid, aluminium chloride, is the most active catalyst. This high reactivity has been amply documented in the EPR literature in the form of various transformations¹⁰ and reinforces earlier caveats regarding the use of AlCl₃ as oxidant. It is also apparent that the acidity of triflic acid is significantly attenuated in nitromethane compared to trifluoroacetic acid; on a molar basis, it is almost 10³ times more active in the latter solvent. Among the strong protic acids the reactivity decreases in the order

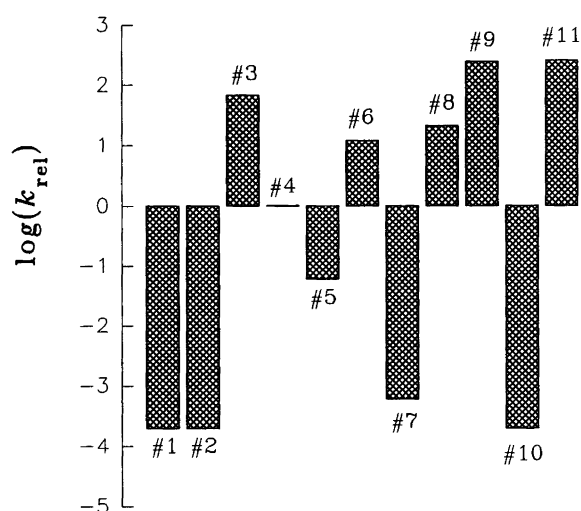


Fig. 2. Bar diagram of some of the rate data reported in Table 2.

CF₃SO₃H > sulfuric acid > perchloric acid, although for the latter the active species must be H₃O⁺.

The use of SbCl₃ as a medium for radical cation generation has been described in a few cases,¹¹ and its characteristics measured here attest to its favourable

properties as a solvent for radical cation EPR spectroscopy. On the other hand, SbCl_5 emerges as an active chlorinating agent, in fact a documented property from early studies,¹² also in connection with EPR spectroscopy,¹³ and applied recently to make highly reactive chlorine-containing species, such as chloronium salts.¹⁴

The reason why the side-reactions mentioned above do not always interfere with the generation of the proper radical cation from any given substrate must reside in favourable thermodynamic factors. If a rearrangement of a substrate takes place, it will give a thermodynamically more stable product, which on the other hand may be less favoured in the oxidation process. As an example, **1** has $E^\circ(\text{ArH}^+/\text{ArH})=1.32\text{ V}$,⁵ whereas $E^\circ(\text{ArH}^+/\text{ArH})$ of **2**, **3** and **4** are 1.45, 1.38 and 1.48 V,¹⁵ respectively. This means that **1** must be almost completely rearranged to **2** before oxidation of **2** starts to compete effectively with that of **1**. In a similar way, the fact that SbCl_5 does give radical cations of the unchanged substrate might be due to the significantly higher $E^\circ(\text{ArH}^+/\text{ArH})$ expected for chlorinated derivatives.

Clearly, the evaluation of Lewis/Brønsted reactivity by the 1→3 rearrangement method is a blunt instrument at the lower limit of reactivity. It would therefore be of interest to develop more sensitive probes to be able to distinguish between the milder reagents.

Experimental

Materials and methods. 1,4,5,8-Tetramethylnaphthalene was prepared from *p*-xylene and γ -valerolactone.¹⁶

EPR spectra were recorded by the Upgrade Version ESP 3220–200SH of a Bruker ER-200D spectrometer. Cyclic voltammetry was performed in dichloromethane– Bu_4PF_6 (0.15 mol dm^{-3}) using a BAS-100 instrument. Reversible potentials were measured at a sweep rate of 0.2 V s^{-1} with an Ag/AgCl electrode as reference. GLC analyses were performed using an HP 5890 series II GLC instrument, equipped with a 25 m OV-1701 capillary column.

General procedure for the acid-catalyzed rearrangement experiments. The acid, either in pure form or dissolved in the appropriate solvent, was added to a stirred solution of 1,4,5,8-tetramethylnaphthalene in nitromethane or dichloromethane, the volume being chosen to get a total volume of 5.0 ml of the final solution. At suitable intervals 50 μl samples were withdrawn and immediately injected into 1.0 ml of saturated aqueous sodium bicarbonate solution to neutralize the acid. The organic components were extracted with 200 μl of pentane, and

the extracts were collected, dried (CaSO_4), and analyzed by GLC.

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