$J = 7$ Hz, $C\mathbf{H}_3CH_2O$, $C\mathbf{H}_3CH_2C{=}O$), 0.86 (d, 6, $J = 6.5$ Hz, $(C\mathbf{H}_3)_2CH$).

Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.09; H, 10.14. Found: C, 64.95; H, 10.27.

Ethyl 6-Methyl-2-methyleneheptanoate (12). A mixture of 0.411 g (1.59 mmol) of diester 11, 0.409 g (3.30 mmol) of DBN, and 10 mL of benzene was stirred and refluxed for 95 h. At the end of this time, GC analysis indicated ca. 15% starting diester still present. An additional 0.2 mL of DBN was added, and refluxing was continued for 23 h. The mixture was cooled, treated with 1 N aqueous HCl and worked up with ether in the usual manner. The oily residue was chromatographed on 50 g of silica gel. Elution with 19:1 hexane–ether gave pure α-methylene ester **12** which was evaporatively distilled. There was obtained 0.241 g (82.4%) of a colorless liquid: bp 80–88 °C (bath temperature) (13 mm); IR 1710 (ester C═O), 1640 cm^{-1} ($CH_2{=}$); NMR δ 6.07 (br s, 1, $CH_2{=}$), 5.43 (br s, 1, $CH_2{=}$), 4.22 (q, 2, $J = 7$ Hz, $OC\mathbf{H}_2CH_3$), 2.29 (br t, 2, allylic CH_2), 1.29 (t, $J = 7$ Hz, $OCH_2C\mathbf{H}_3$), 0.86 (d, 6, $J = 6.5$ Hz, $(C\mathbf{H}_3)_2CH$).

***rac*-Diethyl 3-(4-Methyl-1,2-pentadien-1-yl)-5-(2-methylpropylidene)-1(6)-cyclohexen-1,3-dicarboxylate (17).** To a stirred solution of 0.324 g (1.28 mmol) of allenic diester 14 in 5 mL of anhydrous ether, at −20 °C, was added a solution of 0.25 g (2.02 mmol) of DBN in 1 mL of dry ether. The mixture was stirred at −20 °C for 2 h and was then allowed to warm to 0 °C over 0.5 h whereupon it was treated with 1 N aqueous HCl. Workup with ether in the usual manner gave a pale yellow oil which was chromatographed on 20 g of silica gel. Elution with 9:1 hexane–ether afforded 0.155 g (67.3%) of diester 17 as a pale yellow oil. A sample was evaporatively distilled to give an analytical specimen: bp 100–108 °C (bath temperature) (0.2 mm); IR 1960 (allene), 1722 (ester C═O), 1700 (conj ester C═O), 1630 (C═C), 1610 cm^{-1} (C═C); UV max (95% C_2H_5OH) 275 nm (ϵ 17125); NMR δ 7.50 (br s, 1, CH═), 5.57 (minor isomer), 5.52 (major isomer, 2 d, 1, $J = 9$ Hz, $={\mathbf{C}\mathbf{H}}CH$ of two isomers), 5.20 (m, 2, CH═C═CH), 4.18 (m, 4, $OC\mathbf{H}_2CH_3$), 2.90 (m, 1, $C\mathbf{H}(CH_3)_2$), 2.60–1.45 (br m, 5, allylic CH_2, CH), 1.29, 1.21 (2 t, $J = 6.5$ Hz, $OCH_2C\mathbf{H}_3$), 1.01, 0.95 (2 d, 12, $J = 6.5$ Hz, $(C\mathbf{H}_3)_2CH$) (nonallylic CH_2 not discernible); mass spectrum, m/z 360 (M^+).

Anal. Calcd for $C_{22}H_{32}O_4$: C, 73.30; H, 8.95. Found: C, 73.12; H, 9.16.

Attempted Conversion of 7a to 8a. A solution of 0.339 g (1.49 mmol) of ether ester **7a** and 0.17 mL (2.27 mmol) of propionic acid in 7 mL of toluene was stirred and refluxed for 21 h, cooled, diluted with ether, and treated with saturated aqueous $NaHCO_3$ solution. Workup with ether in the usual manner gave 0.301 g (88.8%) of a pale yellow liquid. Analysis by TLC and GC revealed that this material consisted of only recovered ether ester **7a** with none of the diester **8a** being detectable.

Acknowledgment. We are indebted to the personnel of the Physical Chemistry Department, Hoffmann-La Roche, Inc., Nutley, NJ, for carrying out many of the spectral, microanalytical, and gas chromatographic determinations required during the course of this work.

Registry No. (±)-**1a**, 73262-52-9; **1b**, 52093-38-6; **2**, 42216-96-6; (*E*)-(±)-**7a**, 73262-53-0; (*E*)-(±)-**7b**, 73262-54-1; (*E*)-(±)-**8a**, 73262-55-2; **8b**, 73262-56-3; (*E*)-**9a**, 73262-57-4; (*E*)-(±)-**9b**, 73262-58-5; (±)-**10** (isomer 1), 63568-64-9; (±)-**10** (isomer 2), 73306-83-9; (±)-**11**, 73262-59-6; **12**, 73262-60-9; (±)-**13**, 73262-61-0; (±)-**14** (isomer 1), 73262-62-1; (±)-**14** (isomer 2), 73306-84-0; (±)-**15** (isomer 1), 73262-63-2; (±)-**15** (isomer 2), 73306-85-1; **16** dimer, 73262-71-2; **17**, 73262-64-3; propionic acid, 79-09-4.

Trifluoroacetic Acid Quenching of Naphthalene Fluorescence: Implications for the Mechanism of Photoelectrophilic Hydrogen Exchange

Nigel J. Bunce* and Michael D. Bergsma

Department of Chemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

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The quenching of naphthalene fluorescence by trifluoroacetic acid involves the dimer of the acid. In isooctane, the activation energy for quenching is essentially zero. The previously observed decrease in quenching efficiency in more polar solvents results from their lower dimer content. Hydrogen isotope exchange in the system naphthalene–trifluoroacetic acid–alkane solvent also involves the dimer of trifluoroacetic acid.

Photochemical hydrogen isotope exchange in aromatic compounds is of interest as a rare example of a photochemical electrophilic substitution. In the case of naphthalene, which is the subject of this paper, exchange was first observed by Kuz'min et al.,[1] who used acetic acid/sulfuric acid as the exchange medium. Exchange has been observed also in acetic acid,[2] sulfuric acid,[3] and in alkane solutions of trifluoroacetic acid[4,5] but not in aqueous perchloric acid.[6] These results were reviewed recently.[7]

Hydrogen isotope exchange is a singlet-state reaction, as evidenced by kinetic arguments[1] and a failure to sensitize.[5] In alkane solvents, the fluorescence of naphthalene is quenched by trifluoroacetic acid (TFA), but the efficiency of quenching exceeds the effect of TFA on the quantum yield of hydrogen exchange by a large factor.[5] It was therefore concluded that the initial reaction of TFA with singlet excited naphthalene affords an intermediate in which the incoming and outgoing hydrogen atoms are not equivalent.

The quenching efficiency of TFA is strongly solvent dependent.[5] It is most efficient in alkanes and increasingly less so in benzene, 1-octene, and acetonitrile. In ether and in ethanol no quenching is observed. Since Mataga et al.[8]

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[1] M. G. Kuz'min, B. M. Uzhinov, G. S. Gyorgy, and I. V. Berezin, *Russ. J. Phys. Chem. (Engl. Transl.)*, **41**, 400 (1967).

[2] E. Vander Donckt, D. Lietaer, and J. Nasielski, *Bull. Soc. Chim. Belg.*, **79**, 283 (1970).

[3] C. G. Stevens and S. J. Strickler, *J. Am. Chem. Soc.*, **95**, 3922 (1973).

[4] G. Lodder and E. Havinga, *Tetrahedron*, **28**, 5583 (1972).

[5] N. J. Bunce, Y. Kumar, and L. Ravanal, *J. Org. Chem.*, **44**, 2612 (1979).

[6] S. F. Mason and B. E. Smith, *J. Chem. Soc. A*, 325 (1969).

[7] W. J. Spillane, "Isotopes in Organic Chemistry", Vol. 4, Elsevier, Amsterdam, 1978, p 51.

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Table I. Naphthalene Fluorescence in Various Aerated Solvents

solvent	T, °C	ϕ_F[b]	τ_0, ns
isooctane	2.5	0.028	14.0
isooctane	13.0	0.025	12.6
isooctane	23.0	0.023	11.5
isooctane	40.0	0.021	10.4
isooctane	60.0	0.020	9.9
benzene	23.0	0.062	30.9
1,2-DCE[a]	23.0	0.031	15.2

[a] 1,2-Dichloroethane. [b] Compared with ϕ_F for naphthalene in deoxygenated ethanol.[13,14]

have shown that the lifetime of singlet naphthalene is not strongly solvent dependent, this implies that it is the rate constant for quenching that is being affected by the solvent.

A related question is the basicity of the excited singlet state of naphthalene. Kuz'min et al.[9] found that the singlet excited states of aromatic hydrocarbons are much stronger bases than the corresponding ground states; for naphthalene the pK was 4.0 in the ground state and −16.5 in the excited state[10] relative to liquid HF (eq 1). Since TFA

$$C_{10}H_8 + 2\,HF \overset{K}{\rightleftharpoons} C_{10}H_9^+ + HF_2^- \qquad (1)$$

is a stronger acid than HF in water, we anticipated that excited naphthalene ought to accept a proton from TFA readily. We proposed[5] that this proton transfer has an activation energy which is larger in solvents where TFA is strongly solvated. Then greater solvation would make proton transfer increasingly unlikely within the lifetime of the excited state.

In this paper we report temperature dependent fluorescence quenching studies carried out to test this proposal. From these results we deduce new conclusions about the mechanism of photoelectrophilic hydrogen exchange.

Experimental Section

The spectrofluorimeter was a Hitachi Perkin-Elmer Model MPF-2A equipped with the Model 063-0505 low-temperature accessory. This allows liquid from a thermostatically controlled bath to circulate around the cuvettes. The temperatures recorded were those of the solutions, as measured in the cuvettes, rather than the nominal bath temperatures.

The naphthalene concentration was ca. 10^{-4} M in the ϕ_F measurements and 5×10^{-5} M for the quenching studies; at these concentrations the fluorescence emission intensity is linear with concentration. For the variable-temperature work, the concentrations of naphthalene and of TFA were corrected for expansion or contraction of the solvent by using the compilations of data by Timmermans.[11] All fluorescence intensities were corrected for both Rayleigh and Raman scattering where necessary.

Isooctane was purified as described previously[5] and was free of absorbing or emitting impurities. Commercial 95% ethanol was freed of a fluorescent impurity by refluxing over solid KOH and distillation; the material obtained was treated with quicklime and finally dried by the sodium–ethyl formate method.[12]

Quantum yields of fluorescence (ϕ_F) were determined relative to that of naphthalene in oxygen-free absolute ethanol for which ϕ_F is reported as 0.205[13] and 0.21.[14] Oxygen was removed from the solutions by bubbling dry CO_2 until no further increase in emission intensity was observed. The intensity was compared at the maximum, and since the peak shape and maximum are almost independent of solvent, the intensity was taken to be proportional to ϕ_F. The results for aerated isooctane at different temperatures and for some other solvents are given in Table I, together with the fluorescence lifetimes, by using the relationship[15,16] $\tau/\tau_0 = I/I_0$.

Table II. Fluorescence Quenching of Naphthalene by Trifluoroacetic Acid

T, °C	[TFA], M[a]	I_0/I	T, °C	[TFA], M[a]	I_0/I
		Isooctane			
2.5	0.0105	1.14	40	0.0100	1.09
	0.0209	1.27		0.0200	1.17
	0.0314	1.55		0.0300	1.39
	0.0418	1.82		0.0400	1.50
	0.0628	2.12		0.0600	1.79
	0.0837	2.56		0.0801	2.09
13	0.0103	1.14	60	0.0098	1.07
	0.0207	1.24		0.0195	1.08
	0.0310	1.53		0.0293	1.30
	0.0413	1.68		0.0391	1.35
	0.0620	2.04		0.0586	1.62
	0.0827	2.42		0.0781	1.79
23	0.0102	1.12			
	0.0204	1.20			
	0.0306	1.48			
	0.0409	1.59			
	0.0613	1.92			
	0.0817	2.29			
		Benzene			
23	0.062	1.36	23	0.247	4.81
	0.124	2.24		0.371	8.28
	0.186	3.27		0.618	18.26
		1,2-Dichloroethane			
23	0.096	1.13	23	0.383	3.17
	0.192	1.56		0.575	5.94
	0.288	2.22		0.767	9.71
		Acetonitrile			
23	0.099	1.11	23	0.395	1.47
	0.197	1.25		0.592	1.57
	0.296	1.37		0.789	1.68

[a] Stoichiometric concentration made up at 20.0 °C and corrected for solvent expansion.

Stern–Volmer quenching constants (K_{SV}) were determined by preparing two sets for four solutions for each run. The instrument was used in the ratio mode to allow for variation in the output of the xenon lamp. Values of K_{SV} were determined by a least-squares procedure.

Fluorescence Quenching Studies

The raw quenching data are presented in Table II. Interpretation requires consideration of the dimerization of TFA in the solvents used. Literature data[17,18] indicated that the dimerization constant is high in alkane solvents; since the equilibrium constant for isooctane solvent was unavailable, we used the data of Higazy and Taha[18] in tetradecane as a model and hence calculated the concen-

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[8] N. Mataga, M. Tomura, and H. Nishimura, *Mol. Phys.*, **9**, 367 (1967).

[9] M. G. Kuz'min, B. M. Uzhinov, and I. V. Berezin, *Russ. J. Phys. Chem.* (*Engl. Transl.*), 41, 222 (1967).

[10] Also quoted as −12 in N. J. Turro, "Modern Molecular Photochemistry", W. A. Benjamin, Menlo Park, CA, 1978, p 134.

[11] J. Timmermans, "Physico-Chemical Constants of Pure Organic Compounds", Vol. 1, Elsevier, New York, 1950; *ibid.*, Vol. 2, 1965.

[12] A. I. Vogel, "Practical Organic Chemistry", 3rd ed., Longmans, London, 1956, p 168.

[13] W. R. Dawson and M. W. Windsor, *J. Phys. Chem.*, **72**, 3251 (1968).

[14] B. Stevens and M. Thomaz, *Chem. Phys. Lett.*, **1**, 549 (1968).

[15] Since $\phi_f = k_f/(k_f + k_d) = k_f\tau$, the lifetime is proportional to the quantum yield of fluorescence, since k_f is known[16] to be independent of solvent and of temperature.

[16] J. W. Eastman, *Spectrochim. Acta, Part A*, **26**, 1545 (1970).

[17] S. D. Christian and T. L. Stevens, *J. Phys. Chem.*, **76**, 2039 (1972).

[18] W. S. Higazy and A. A. Taha, *J. Phys. Chem.*, **74**, 1982 (1970).

Table III. Correlation of Naphthalene Fluorescence Quenching with TFA Monomer and Dimer Concentrations

solvent	T, °C	K^a	monomer $K_{SV}{}^c$	monomer correl coeff	dimer $K_{SV}{}^c$	dimer correl coeff	k_Q,^{e} L mol^{-1} s^{-1}
isooctane	2.5	19000	978	0.9361	38.3	0.9968	2.74×10^9
isooctane	13.0	5700	494	0.9367	35.8	0.9976	2.84×10^9
isooctane	23.0	1940	264	0.9345	33.4	0.9968	2.90×10^9
isooctane	40.0	347	101	0.9413	31.5	0.9982	3.01×10^9
isooctane	60.0	60.3	35	0.9442	29.1	0.9928	2.94×10^9
benzene	23.0	2.6	58.5	0.9087	95.6	0.9941	3.09×10^9
1,2-DCE^b	23.0	1.5	21	0.8944	41.4	0.9862	2.72×10^9
CH_3CN	23.0	$<0.03^d$	0.93	0.9813	37.2	0.8814	

^{a} Dimerization constant. ^{b} 1,2-Dichloroethane. ^{c} Stern–Volmer quenching constant = $k_Q\tau$. ^{d} Assumed, see footnote 19. ^{e} $k_Q = K_{SV}(\text{dimer})/\tau$.

trations of monomeric and dimeric TFA in solution. In an attempt to correlate the fluorescence intensity ratio (eq 2) with Q = TFA monomer or Q = TFA dimer, it was clear that in isooctane the active quencher is the dimer of TFA rather than the monomer (Table III).

$$I_0/I_Q = 1 + k_Q\tau[Q] \qquad (2)$$

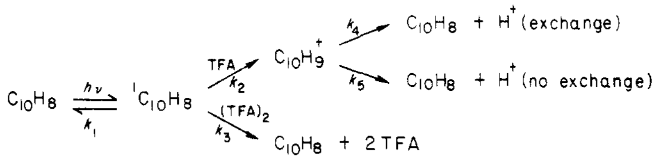
In eq 2, the lifetime τ is that of the unquenched naphthalene under the prevailing reaction conditions, i.e., aerated solution at the appropriate temperature. With the values of τ from Table I, we calculated the rate constant k_Q for quenching by the dimer, shown as the last column in Table III.

Isooctane is not unique as a solvent in which quenching of naphthalene fluorescence is by a TFA dimer. Benzene and 1,2-dichloroethane both have very much lower equilibrium constants for TFA dimerization;[17] in both these solvents the dimer is the active quencher. Acetonitrile represents a possibly exceptional case; quenching is very inefficient in this solvent but seems consistently to correlate with the monomer concentration.[19,20]

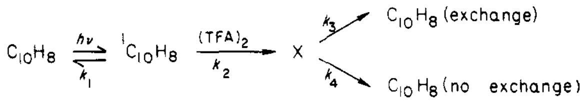
Returning to the data in isooctane, an Arrhenius plot of log k_Q vs. $1/T$ afforded the activation parameters E_a = 1.1 ± 0.4 kJ mol^{-1} and log A = 9.64 ± 0.07. Thus the energy of activation is essentially zero,[21,22] and the value of log A is only slightly lower than that for "typical" bimolecular reactions in solution.[23] Thus there seems to be little orientational requirement for a collision between TFA dimer and singlet excited naphthalene to lead to quenching of the excited state.

These results refute our earlier proposition[5] that the solvent effect in fluorescence quenching results from an activation energy which is larger in more highly solvating solvents. Instead, we see essentially zero activation energy, and the solvent effect results simply from the lower TFA dimer content in more highly solvating media. In hydrogen bonding solvents such as ethers and alcohols, the dimer content is so low that no quenching is observed. Moreover, in the three solvents for which the actual value of k_Q was deduced, it is almost independent of solvent.

Scheme I



Scheme II



What is the chemical nature of fluorescence quenching? The following facts suggest the involvement of proton transfer: small kinetic isotope effect and quenching observed in isooctane only for strong Brønsted acids such as trifluoroacetic, trichloroacetic, and *p*-dodecylbenzenesulfonic.[5] Yet it is difficult to understand why the dimer should be a better proton donor than the monomer as indicated by the correlation of K_{SV} in solvents such as benzene and 1,2-dichlorethane, where the amounts of monomer and dimer present in the solutions were comparable. The fact that the dimer quenches suggests that quenching might involve exciplex formation with some degree of electron transfer from naphthalene to the dimeric acid. Then the requirement for a strong Brønsted acid would be coincidental: the electron-withdrawing groups that make TFA a strong Brønsted acid also make it a good electron acceptor. There is the additional problem that the nature of the TFA dimer is somewhat controversial; it has been suggested that the dimer may be linear instead of the conventional cyclic structure found for carboxylic acids such as acetic acid.[20,24,25] In short, the chemical nature of quenching cannot be unequivocally deduced at present, although the lack of a solvent effect on k_Q might argue in favor of formation of an exciplex with relatively little electron-transfer character.

Mechanism of Photoelectrophilic Hydrogen Exchange

The finding that TFA dimer quenches the fluorescence of naphthalene raises the possibility that in alkane solvents, photoelectrophilic hydrogen exchange may be unrelated to fluorescence quenching. Although both proceed from the singlet state, the former might involve monomeric TFA and the latter the dimer. Alternatively, both processes could involve the dimer. Schemes I and II (where

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(19) The value of the TFA dimerization constant has apparently not been determined in acetonitrile. Kirszenbaum et al.[20] could not detect $\nu_{C=O}$ for the TFA dimer in this solvent. In dichloroethane at 1.0 M TFA, the intensities of $\nu_{C=O}$(dimer) and $\nu_{C=O}$(monomer) were equal, and the association constant is known[17] to be 1.5. Assuming that $\nu_{C=O}$(dimer) could have been seen if it was 5% as intense as $\nu_{C=O}$(monomer), we can calculate an upper limit for the association constant in acetonitrile as 0.03, using moles per liter as the units.

(20) M. Kirszenbaum, J. Corset, and M. L. Josien, *J. Phys. Chem.*, **75**, 1327 (1971).

(21) In fact, it is less than would be calculated as an apparent activation energy resulting from increasing collision frequency as the viscosity of isooctane changes with temperature.[22]

(22) K. M. Khalilov, *Russ. J. Phys. Chem.* (*Engl. Transl.*), **36**, 1341 (1962).

(23) W. J. Moore, "Physical Chemistry", 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1972, p 406.

(24) T. S. S. R. Murty and K. S. Pitzer, *J. Phys. Chem.*, **73**, 1426 (1969).

(25) I. S. Perelygin and A. M. Afanas'eva, *Zh. Strukt. Khim.*, **14**, 1033 (1973); *Chem. Abstr.*, **80**, 70154 (1974).

$^1C_{10}H_8$ indicates the singlet state) outline appropriate mechanistic possibilities.[26]

In Scheme II, X could result from either proton or electron transfer, as mentioned above. If electron transfer is involved, then a subsequent transfer of a hydrogen atom would be required for hydrogen exchange to occur. The appropriate expressions for ϕ_{ex}, the quantum yield of hydrogen exchange, are given as eq 3 for Scheme I and eq 4 for Scheme II. In these equations, [M] and [D] refer to monomeric and dimeric TFA concentrations, respectively.

$$\phi_{ex} = \left(\frac{k_4}{k_4 + k_5}\right)\left(\frac{k_2[M]}{k_1 + k_2[M] + k_3[D]}\right) \qquad (3)$$

$$\phi_{ex} = \left(\frac{k_3}{k_3 + k_4}\right)\left(\frac{k_2[D]}{k_1 + k_2[D]}\right) \qquad (4)$$

We argue in favor of the second possibility as follows. Equation 3 can be transformed into eq 5, where $\alpha = k_4/(k_4 + k_5)$. Since ϕ_r is found experimentally to increase with the stoichiometric concentration of TFA[5,27] the value of $\phi_r/(\alpha - \phi_r)$ increases with [TFA]. Likewise, the value of $(1 + K_{SV}K[M]^2)/[M]$ must increase with increasing [TFA]. Consequently, this model can never compute a constant value for $k_2\tau$, and in practice the calculated value of $k_2\tau$ rises monotonically with [TFA].

$$k_2\tau = \left(\frac{\phi_r}{\alpha - \phi_r}\right)\left(\frac{1 + K_{SV}K[M]^2}{[M]}\right) \qquad (5)$$

By contrast, a good fit to Lodder's data[27] ($r = 0.997$) is found when $1/\phi_{ex}$ is plotted against 1/[D] as required by eq 4. Scheme II thus accounts for the experimental data.

Spillane[7] has raised the question that it may be the excimer of naphthalene that undergoes hydrogen exchange rather than the monomeric singlet. This possibility is clearly excluded by Lodder's data,[27] which show the relationship $1/\phi_{ex} \propto [C_{10}H_8]$, which is to be expected if the monomer is reactive and the excimer unreactive. The reverse situation leads to a linear relationship between $1/\phi_{ex}$ and $1/[C_{10}H_8]$.

We conclude that both fluorescence quenching and hydrogen exchange in the system naphthalene–TFA in alkane solvents involve the dimer of TFA and not the monomer. Further insight into the mechanism of hydrogen exchange in this system must await more information on the nature of the intermediate formed in the initial interaction between the TFA dimer and the naphthalene singlet.

Acknowledgment. We thank the NSERC of Canada for financial support, Professor E. Havinga for kindly making available a copy of the thesis of G. Lodder, and Drs. R. K. Boyd and S. Goldman for helpful discussions.

Registry No. Naphthalene, 91-20-3; TFA, 76-05-1; TFA dimer, 40857-16-7.

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[26] For simplicity, the reverse of the quenching steps whose rate constants are k_2 and k_3 (Scheme I) and k_2 (Scheme II) are omitted.

[27] G. Lodder, Thesis, University of Leiden, 1971, pp 110–3. The thesis provides the raw data on which the graphs of ref 4 are based.

Pyrolysis of Nitrobenzene

Edward McCarthy* and Kennedy O'Brien

Corporate Research Center, Allied Chemical Corporation, Morristown, New Jersey 07960

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The pyrolysis of nitrobenzene was examined over the temperature range of 275–630 °C. Liquid products were determined by using a GC–MS combination. Evaluation of the gaseous products was done by using an on-line IR gas cell. At the lower temperatures, nitrobenzene decomposes via direct rupture of the arene–nitro bond to give phenyl radical and NO_2 as primary products. As the temperature is raised, the yield of NO_2 decreases.

There still exists uncertainty on the question of what are the primary products resulting from the pyrolysis of nitrobenzene. Two reports highlight this question. In the earlier report,[1] Fields and Meyerson, utilizing a flow-through Vycor reactor, postulated that at 600 °C the nitro–arene bond breaks to produce phenyl radical and nitrogen dioxide. This was based on the distribution of liquid products obtained from the pyrolysis and from the similarity of this distribution to the mass spectrum. In the mass spectrum, m/e 77, $C_6H_5^+$ is the base peak of the spectrum and m/e 77 and 123, the molecular ion for nitrobenzene, are related by a metastable transition. Although noncondensable gases were caught in a gas bulb for analysis and analyzed with a mass spectrometer, nitrogen dioxide was not detected. However, given the difficulty experienced by Friedel in analyzing for NO_2 with a mass spectrometer,[2] its absence is not too surprising. In a parallel study,[3] nitrobenzene was examined over the temperature range 400–600 °C by utilizing a stainless-steel-tube reactor on-line with a gas chromatograph. The effluent of the chromatograph was allowed to flow directly into a mass spectrometer. Here, no nitrogen dioxide was detected. Its absence was established by monitoring m/e 46, the molecular ion of nitrogen dioxide, during passage of the effluent through the mass spectrometer. (It was also necessary to simultaneously monitor m/e 44, the molecular ion of carbon dioxide. The latter, ever-present in a pyrolysis, would contribute to m/e 46 via the species $CO^{16}O^{18}$.) From the variation of the concentration of nitrosobenzene, one of the products of pyrolysis, with temperature and the similarity of the distribution of products to those obtained from the pyrolysis of nitrosobenzene

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[1] E. K. Fields and S. Meyerson, *J. Am. Chem. Soc.*, **89**, 3224 (1967).

[2] R. A. Friedel, A. G. Sharkey, J. L. Shultz, and C. R. Humbert, *Anal. Chem.*, **25**, 1314 (1953).

[3] C. W. Hand, C. Merritt, Jr., and C. DiPietro, *J. Org. Chem.*, **42**, 841 (1977).