1215. *Kinetics of the Addition of Tetrafluorohydrazine to Polycyclic Aromatic Hydrocarbons*

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The reaction of tetrafluorohydrazine with polycyclic aromatic hydrocarbons was studied in " iso-octane " as a solvent at 40·0°. The reaction is second-order (first-order in both substrate and tetrafluorohydrazine). The observed sequence of reactivity, anthracene > *trans*-stilbene > 1,2-benzanthracene > phenanthrene > naphthalene, is discussed in terms of three types of addition mechanism. Pyrolysis at 220° of the bisdifluoro-amino-adducts of *trans*-stilbene and anthracene leads mainly to the formation of the parent aromatic hydrocarbon.

In tetrafluorohydrazine, detectable amounts of difluoroamino radicals are present at ambient temperatures, owing to the low N–N bond strength.[1] Participation of tetrafluorohydrazine in free-radical reactions (possibly involving the difluoroamino radical) have been reported.[2] The gas-phase reaction of tetrafluorohydrazine with alkenes in fact takes place as a two-step addition of difluoroamino radicals.[3] The present work describes the kinetics of the reaction of tetrafluorohydrazine with *trans*-stilbene and some fused aromatic hydrocarbons in " iso-octane " as solvent.

Experimental

Materials.—Tetrafluorohydrazine was obtained from Air Products, U.S.A. Phenanthrene (Fluka) was freed from anthracene by treating it twice with maleic anhydride.[4] The other aromatic hydrocarbons (B.D.H., *puriss.*) were used without further purification. B.D.H. spectrograde Iso-octane was purified by passing it through a 150-cm. activated silica gel (30—100 mesh) column to remove traces of unsaturated compounds.[5] Two batches of " iso-octane " have thus been purified. The first was unreactive towards tetrafluorohydrazine; the second, employed for 1,2-benzanthracene only, reacted very slowly with tetrafluorohydrazine, and corrections have been applied.

Procedure.—The solution of an aromatic hydrocarbon in " iso-octane " was deaerated at room temperature in a burette at a hydrogen pressure of ∼50 mm. by bubbling hydrogen through this solution for 2 min. The burette was attached to a conventional high-vacuum system. A reaction flask, provided with a break-seal, was evacuated to less than 10^{-4} mm. Thereupon a known volume of the deaerated solution (for the kinetic runs 8·32 ml.) was transferred to the reaction flask. The contents were cooled at liquid-air temperature, and the reaction flask

[1] F. A. Johnson and Ch. B. Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.
[2] J. P. Freeman, A. Kennedy, and Ch. B. Colburn, *J. Amer. Chem. Soc.*, 1960, **82**, 5304; R. C. Petry and J. P. Freeman, *ibid.*, 1961, **83**, 3912.
[3] A. J. Dijkstra and A. F. Trotman-Dickenson, personal communication.
[4] W. E. Bachman and M. C. Kloetzel, *J. Amer. Chem. Soc.*, 1938, **60**, 481.
[5] C. Steel and M. Szwarc, *J. Chem. Phys.*, 1960, **33**, 1677.

evacuated. A known amount of gaseous tetrafluorohydrazine was condensed into the reaction cell, which was then sealed. The reaction flask was immersed in a water-bath kept at $40 \cdot 0 \pm 0 \cdot 1°$ and shaken continuously with a vibro-shaker. After an appropriate reaction time the flask was removed from the water-bath, its contents were frozen immediately at liquid-air temperature, and the amount of unconverted tetrafluorohydrazine was determined with an analytical line. This high-vacuum line consisted of a Dewar type of trap, an absorption tube with polyethylene glycol 400 (B.D.H.) on firebrick (Fossalsil; 30—40 mesh) to remove possible traces of difluoroamine, a Ward still, a Toepler pump, and a gas-burette which was connected *via* a stopcock to a small freezing-bulb. The reaction flask was attached to a ground joint linked to the Dewar type of trap. The latter was cooled to $-73°$, the Ward still to $-140°$, and the freezing-bulb to liquid-air temperature. The analytical line was evacuated to less than 10^{-4} mm. Thereupon the break-seal of the reaction flask was broken with a magnetic hammer. By removing the liquid-air bath, the contents of the reaction flask were allowed to distil. The bulk of " iso-octane " was collected in the trap, the residual traces in the Ward still, and the unconverted tetrafluorohydrazine in the freezing bulb. The amount of tetrafluorohydrazine was determined by expansion of the contents of the freezing-bulb into the gas-burette.

Reaction Products.[*] With *trans*-stilbene and anthracene, the product formed in the presence of excess of tetrafluorohydrazine after a prolonged reaction time was isolated by removing the residual hydrazine and the solvent under reduced pressure.

1,2-*Bisdifluoroamino*-1,2-*diphenylethane* (Found: C, $60 \cdot 0$; H, $4 \cdot 1$; F, $26 \cdot 7$; N, $8 \cdot 9$. $C_{14}H_{12}F_4N_2$ requires C, $59 \cdot 2$; H, $4 \cdot 3$; F, $26 \cdot 7$; N, $9 \cdot 9\%$) was formed from *trans*-stilbene by uptake of an equimolar amount of tetrafluorohydrazine (cf. Figure 1). The addition compound decomposes above $80°$ with evolution of gas. Its n.m.r. spectrum, measured in deuterochloroform at $40°$, exhibited two triplets at $\tau = 4 \cdot 75^6$ ($J = 23 \cdot 5$ c./sec.) and $\tau = 5 \cdot 00$ ($J = 24 \cdot 5$ c./sec.), respectively, and a complex multiplet centred at $\tau \sim 2 \cdot 8$. The multiplet is assigned to the phenyl hydrogens and the two triplets to the benzylic hydrogens, the ratio of the areas of the two triplets to the multiplet being $0 \cdot 19$ (required $0 \cdot 20$). The triplet splitting is due to fluorine–hydrogen coupling in the H–C–N–F group. In the aliphatic series the hydrogen–fluorine coupling constant is 28 c./sec.[7] The observation of two triplets may be explained by the presence of (1) a mixture of the *meso*-compound and the racemic mixture, or (2) two conformations of either the *meso*-compound or the recemic mixture. The mass spectrum, obtained with the heated inlet system at $65°$ (Table 1), showed a parent peak of low intensity at $m/e = 284$ (required 284). The fragmentation pattern is conceivable with the proposed structure of the adduct.

9,10-*Bisdifluoroamino*-9,10-*dihydroanthracene* (Found: C, $61 \cdot 4$; H, $3 \cdot 8$; N, $10 \cdot 2$. $C_{14}H_{10}F_4N_2$ requires C, $59 \cdot 6$; H, $3 \cdot 6$; N, $9 \cdot 9\%$) was formed from anthracene by uptake of an equimolar amount of tetrafluorohydrazine (cf. Figure 1). The addition compound decomposes above $130°$ with gas evolution. Its n.m.r. spectrum, measured in deuterochloroform at $40°$, showed two triplets at $\tau = 4 \cdot 20$ ($J = 24 \cdot 0$ c./sec.) and $\tau = 4 \cdot 39$ ($J = 25 \cdot 8$ c./sec.), and a complex absorption pattern of two overlapping multiplets centred at $\tau \sim 2 \cdot 3$ and $\sim 2 \cdot 5$, respectively. The intensity of the triplet at $\tau = 4 \cdot 39$ is weak in comparison with that of $\tau = 4 \cdot 20$. The multiplet is assigned to the phenylene hydrogens, the triplets to the aliphatic hydrogens, the observed ratio of the areas of the sum of the two triplets to the multiplet being $0 \cdot 26$ (required $0 \cdot 25$). The observation of two triplets agrees with the presence of (1) a mixture of *cis*- and *trans*-addition product, (2) a *cis*-addition product, or (3) a *trans*-addition product. As to the last possibility, this would give rise to two triplets of equal intensity, as one of the aliphatic hydrogens will have the " axial " and the other the " equatorial " position.[†] The observed unequal intensity of the two triplets accordingly rules out the presence of only the *trans*-addition product.

† In 9,10-dihydroanthracene the central ring has the boat conformation and the planes of the two phenylene rings make an angle of $\sim 145°$.[8] This geometry gives rise to " axial " and " equatorial "[9] methylene hydrogens.

[6] G. V. D. Tiers, *J. Phys. Chem.*, 1958, **62**, 1151.
[7] C. L. Bumgardner, *Tetrahedron Letters*, 1964, 3683.
[8] W. G. Ferrier and S. Iball, *Chem. and Ind.*, 1954, 1296; A. H. Beckett and B. A. Mulley, *ibid.*, 1955, 146.
[9] D. Y. Curtin, C. G. Carlson, and C. G. McCarty, *Canad. J. Chem.*, 1964, **42**, 565.

The mass spectrum, obtained with the heated inlet system at 110° (Table 1) showed a parent peak of very weak intensity at $m/e = 282$ (required 282). The presence of the imide peaks at $m/e = 242$ and 223 is easily understood with the proposed structure of the adduct.

Pyrolysis of Bisdifluoroamino-adducts.—According to the observed mass spectra (Table 1), pyrolysis at 220° of 1,2-bisdifluoroamino-1,2-diphenylethane leads to a mixture of mostly *trans*-stilbene (ratio of the peak heights at $m/e = 180, 179, 178, 165,$ and 152 about similar to that of an authentic *trans*-stilbene sample), with some αα'-bisdifluoroaminostilbene (cf. peaks at $m/e = 281, 206$—204) and benzonitrile (ratio of the peak heights at $m/e = 103, 77, 76$ similar to that of benzonitrile; apparently the contribution of the fragment C_8H_7 to the peak at $m/e = 103$ is small).

With 9,10-bisdifluoroamino-9,10-dihydroanthracene at 220°, the main pyrolysis product is anthracene (peak heights ratio at $m/e = 178, 177,$ and 176 similar to that of an authentic sample). During the initial stages of the pyrolysis the intensities of the peaks $m/e = 52$ and 33 are strongly increased, indicating the presence of difluoroamino radicals.[10] A similar pyrolysis pattern was reported [11] for " 9,10-di-cyanoisopropyl-9,10-dihydroanthracene."

RESULTS

Kinetics.—The reaction of aromatic hydrocarbons with tetrafluorohydrazine was studied at 40·0° in " iso-octane " as a solvent. At 40·0° the vapour pressure of the aromatic hydrocarbons studied is negligible. The possibility that part of the reaction takes place in the gas phase can therefore be excluded.

TABLE 1

Mass spectra of tetrafluorohydrazine adducts*

	trans-Stilbene adduct				Anthracene adduct		
		Rel. intensity				Rel. intensity	
m/e	Assigned fragment	65°	220° †	m/e	Assigned fragment	110°	220° †
76	C_6H_4	29	695	176	$C_{14}H_8$	47	17
77	C_6H_5	22	152	177	$C_{14}H_9$	16	9·7
103	C_6H_5CN; C_8H_7	42	2140	178	$C_{14}H_{10}$	36	100
142	$C_6H_5\cdot CHNF_2$	12	—		CNF		
152	$C_{12}H_8$	3·7	8·9	223	$C_6H_4 \qquad C_6H_4$	77	0·5
165	$C_{13}H_9$	20	40		CN		
178	$C_6H_5\cdot C\!:\!C\cdot C_6H_5$	19	68		CNF		
179	$C_6H_5\cdot CH\!:\!C\cdot C_6H_5$	39	97	241	$C_6H_4 \qquad C_6H_3$	21	—
180	$C_6H_5\cdot CH\!:\!CH\cdot C_6H_5$	100	100		CNF		
198	$C_6H_5\cdot CH\!:\!CF\cdot C_6H_5$	—	17		CNF		
204	$C_{14}H_8N_2$	—	6·1	242	$C_6H_4 \qquad C_6H_4$	100	—
205	$C_{14}H_9N_2$	1·4	4·0		CNF		
206	$C_{14}H_{10}N_2$	0·6	4·7		CHNF_2		
232	$C_6H_5\cdot CH\cdot CHNF_2\cdot C_6H_5$	10·3	—	282	$C_6H_4 \qquad C_6H_4$	0·04	—
281	$C_6H_5\cdot CNF_2\!:\!CNF_2\cdot C_6H_4$	—	1·9		CHNF_2		
284	$C_6H_5\cdot CHNF_2\cdot CHNF_2\cdot C_6H_5$	0·7	—				

* Only major peaks and peaks of structural interest have been tabulated. The acclerating voltage of the bombarding electrons was 70 ev.   † Spectra recorded after 1 hour's pyrolysis in the heated inlet system at 220°.

The consumption of tetrafluorohydrazine was studied for *trans*-stilbene and anthracene. In the case of prolonged reaction times, 1 mole of tetrafluorohydrazine is consumed per mole of hydrocarbon (Figure 1). Series of experiments with a ten-fold excess of aromatic hydrocarbon showed the reaction to be first-order with respect to tetrafluorohydrazine. Typical plots are shown in Figure 2. The pseudo-first-order rate constants, calculated from these plots, vary linearly with the concentration of the aromatic hydrocarbon. Apparently the reaction under study is governed by the stoicheiometric equation, $A + N_2F_4 \longrightarrow AN_2F_4$ where A represents an aromatic hydrocarbon. Consequently,

$$d[A] = -k_2[A][N_2F_4]dt.$$

[10] J. T. Herron and V. H. Dibeler, *J. Chem. Phys.*, 1960, **33**, 1594; C. W. Schoenfelder, *J. Chromatog.*, 1962, **7**, 281.
[11] A. F. Bickel and E. C. Kooyman, *Rec. Trav. chim.*, 1952, **71**, 1137.

A complicating factor arises from the fact that only part of the tetrafluorohydrazine is present in the liquid phase:

$$(N_2F_4)_{total} = [N_2F_4]_{liq}V_{liq} + [N_2F_4]_{vap}V_{vap}$$

For a given temperature, according to Henry's law,

$$[N_2F_4]_{vap}/[N_2F_4]_{liq} = c.$$

Accordingly, it follows that

$$\frac{k_2}{V_{liq} + cV_{vap}} = \frac{2 \cdot 303}{\{(N_2F_4)_{total\ 0} - A_0\}t} \log \frac{(N_2F_4)_{total}A_0}{(N_2F_4)_{total\ 0}A}$$

where the subscript zero refers to zero time. Values of $k_2/(V_{liq} + cV_{vap})$ are given in Table 2. V_{liq} was constant in all experiments (8·32 ± 0·02 ml.), whereas V_{vap} varied slightly from one experiment to another, the average value being 5·4 ml. with a standard deviation of 0·6 ml.
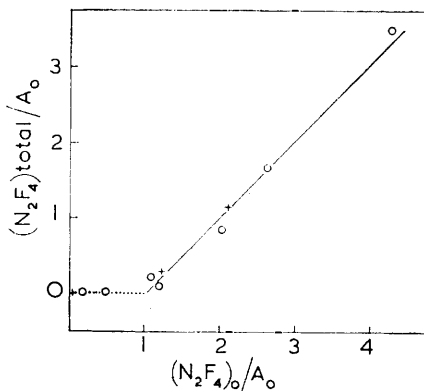
FIGURE 1. Consumption of tetrafluorohydra-zine in its reaction with *trans*-stilbene (+) and anthracene (O) at 40·0°
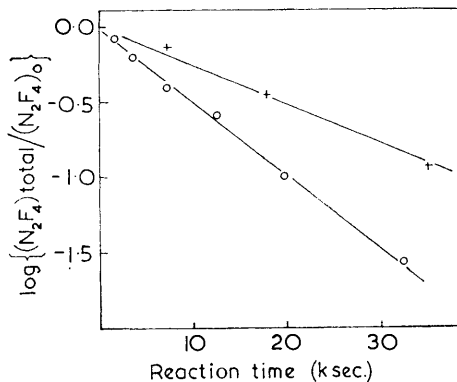
FIGURE 2. Addition of tetrafluorohydrazine to aromatic hydrocarbons at 40·0°. + 0·408 mmole of *trans*-stilbene and 0·0230 mmole of N_2F_4; O 0·0382 mmole of anthracene and 0·0059 mmole of N_2F_4

TABLE 2

Relative rates of reaction of aromatic hydrocarbons with tetrafluorohydrazine in " iso-octane " as solvent at 40·0°

Hydrocarbon	t (ksec.)	10^3A_0 (mmoles)	$10^3(N_2F_4)_0$ (mmoles)	$10^3k_2/(V_{liq} + cV_{vap})$ (ksec.$^{-1}$)
Naphthalene	162·7	5590	24·0	0·0131
	318·8	5550	26·9	0·0155
trans-Stilbene	7·2	409	23·1	105
	18·0	408	22·6	146
	35·1	407	23·0	157
	25·2	198	18·3	137
Anthracene	7·20	38·4	5·99	3500
	32·4	38·2	5·94	3290
	12·66	15·5	5·98	3300
	1·80	74·9	5·94	3380
Phenanthrene......................	590·4	324	5·93	1·29
	595·8	219	5·94	0·73
	1242	220	5·99	0·86
	857	220	5·94	1·09
1,2-Benzanthracene	46·9	51·9	4·66	24 (48 *)
	166·2	53·3	4·85	20 (53 *)
	253·2	53·4	4·91	21 (55 *)

* Not corrected for N_2F_4 consumption by the solvent.

c is a constant of unknown value (for methylene chloride at $40°$ $c = 0.8$ [12]). Thus, the factor $(V_{liq} + cV_{vap})$ is approximately constant for all experiments. Consequently $k_2/(V_{liq} + cV_{vap})$ is a measure of the relative reactivity of the various hydrocarbons.

DISCUSSION

As to the nature of polycyclic aromatic hydrocarbons and the observed first-order kinetics in both the substrate and tetrafluorohydrazine, three mechanisms can be considered, *i.e.*, a radical addition, a concerted one-step addition, and an electrophilic addition.

A radical addition will proceed by the steps (1)—(3)

$$N_2F_4 \rightleftharpoons 2 \cdot NF_2 \qquad (1)$$

$$A + \cdot NF_2 \rightleftharpoons \cdot ANF_2 \qquad (2)$$

$$\cdot ANF_2 + \cdot NF_2 \longrightarrow F_2NANF_2 \qquad (3)$$

For the experiments of Table 2 the $|\cdot NF_2|/|N_2F_4|$ ratio will be between 0.1 and 0.04, provided that the equilibrium constant K_1 in " iso-octane " does not differ greatly from that [1] in the gas phase, and that $c \sim 1$. Thus, $|\cdot NF_2| \sim \sqrt{K_1 | N_2F_4 |}$ stoich. In order to compy with the observed first-order kinetics in tetrafluorohydrazine, reaction (3) has to be rate-determining, *i.e.*, $k_3 |\cdot NF_2| \ll k_{-2}$. For the reactions (1)—(3) it follows then that

$$v = (k_2k_3/k_{-2})|A| |\cdot NF_2|^2 \sim (k_2k_3/k_{-2})K_1 |A| | N_2F_4 |_{stoich}$$

With methyl [13] and trichloromethyl [14] radicals, the addition of the first radical is thought to be rate-determining. Accordingly, a linear correlation between the tetrafluorohydrazine reactivity data and those of methyl and trichloromethyl is not to be expected, and is in fact not observed (Table 3).

Secondly, a one-step concerted molecular-addition mechanism may be considered. It has been proposed [15-17a] that the rate of such a reaction depends mainly on the energy required to localise two of the π-electrons on the appropriate pair of carbon atoms. This localisation energy, L, is equal to the difference in resonance energy between the starting hydrocarbon and the reaction product. The lowest localisation energies for 1,2- and 1,4-addition, calculated from reported [17b] resonance energies, as well as the derived overall rate constants at $40°$, are collected in Table 3. The correlation between the calculated and observed rate constants is not satisfactory, especially for *trans*-stilbene.

Finally, in the case of an electrophilic addition mechanism tetrafluorohydrazine should act as electrophile. This is conceivable, as fluorine is more electronegative than nitrogen.

$$A + N_2F_4 \rightleftharpoons A^+ - NF_2 \ NF_2^- \qquad (4)$$

$$A^+ - NF_2 \ NF_2^- \longrightarrow F_2NANF_2 \qquad (5)$$

In order to comply with the octet rule, the intermediate is likely to be an ion-pair, although intermediates involving expanded octets of chlorine have been discussed [18] in electrophilic aromatic chlorination. The conversion of the ion pair intermediate into the final adduct

[12] Ch. B. Colburn, personal communication.
[13] F. Leavitt, M. Levy, M. Szwarc, and V. Stannett, *J. Amer. Chem. Soc.*, 1955, **77**, 5493; M. Szwarc and J. H. Binks, " Theoretical Organic Chemistry," *Chem. Soc. Special Publ.*, No. 12, 1959, p. 269.
[14] E. C. Kooyman and E. Farenhorst, *Trans. Faraday Soc.*, 1953, **49**, 58.
[15] R. D. Brown, *Austral. J. Sci. Res.*, 1949, *A*, **2**, 564.
[16] R. D. Brown, *J.*, 1950, 691; 1951, 1612; M. J. S. Dewar, *J. Amer. Chem. Soc.*, 1952, **74**, 3357; R. Daudel, R. Lefebre, and C. Moser, " Quantum Chemistry," Interscience, London, 1959, p. 257.
[17] G. W. Wheland, " Resonance in Organic Chemistry," Wiley, New York, 1955, (*a*) p. 376; (*b*) pp. 80 and 98.
[18] P. B. D. de la Mare, N. V. Klassen, and R. Koenigsbergen, *J.*, 1961, 5285.

is likely to be fast in comparison to its formation. Accordingly, a linear correlation may be expected between the logarithm of the partial rate constant and the cation-localisation energy L_r^+,[19] or the electrophilic substitution constant, σ_r,[19] which is defined relative to a single α-position in naphthalene for protonation as the standard reaction. The observed reactivity sequence is that predicted by σ_r. Quantitatively, however, the correlation is far from satisfactory.

TABLE 3

Relative reactivities of aromatic hydrocarbons towards tetrafluorohydrazine at 40·0°

Hydrocarbon	Observed		Radical addition Log k_1 *		Concerted molecular addition			Electrophilic addition		
	Log k *	Positions of addition	·CH$_3$ [13]	·CCl$_3$ [14]	Positions of attack	L (kcal./ mole)	Log $k_{calc.}$*	Positions of attack	σ_r [19]	L^+_r/β [19]
Naphthalene	0·00		0·00	0·00	1, 2	22·9	0·0	1	0·0	2·299
					1, 4	25·0	−1·7	2	−3·4	2·480
Anthracene	5·38	9, 10	1·69	2·74	1, 2	20·4 †	1·8	1	1·1	2·25
					1, 4	22·5	0·7	2	0·0	2·40
					9, 10	11·5	7·4	9	8·1	2·013
Phenanthrene	1·8		−0·21	−0·40	1, 2	28·2 †	−4·0	1	0·2	2·318
					3, 4	28·2	−4·0	4	−0·5	2·366
					9, 10	20·3	1·2	9	0·5	2·299
1,2-Benzanthracene	3·2		1·37	2·87	5, 6	15·6 ‡	4·5	7	6·6	2·101
					8, 9	18·2 †	2·7	12	6·6	2·049
					10, 11	18·2 †	2·7			
					7, 12	14·6	5·2			
trans-Stilbene	3·9	$\alpha\alpha'$	0·49	1·40	$\alpha\alpha'$	7·0	10·5			
					2, 3	21·9 §	0·7			

* Overall rate constants, expressed relative to naphthalene.   † The increase in resonance energy on introduction of a vinyl group into a polycyclic aromatic hydrocarbon was taken as equal to the overall difference of styrene and benzene, *i.e.*, 2 kcal./mole.   ‡ The resonance energy of 2-phenylnaphthalene was taken as 96 kcal./mole (cf. diphenyl [17b]).   § The resonance energy of 1-phenylhexa-1,3,5-triene was taken as 57 kcal./mole.[15]

The discussion given above illustrates that as yet no mechanisitic assignment can be made. Determination of the stereochemistry of the tetrafluorohydrazine addition to the various compounds seems of vital interest for further elucidation of the reaction mechanism(s).

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[19] A. Streitwieser, jun., " Molecular Orbital Theory," Wiley, New York, 1961, pp. 326 and 335.