767. *Collision Diameters of Flexible Hydrocarbon Molecules in the Vapour Phase: The "Hydrogen Effect."*

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Mass-diffusion measurements have been carried out by the Stefan method, with hydrogen, nitrogen, oxygen, and argon as carrier gases, at temperatures convenient for the following hydrocarbons: *n*-hexane, 2 : 3-dimethylbutane, *cyclo*hexane, methyl*cyclo*pentane, *n*-octane, 2 : 2 : 4-trimethylpentane, *n*-decane, 2 : 3 : 3-trimethylheptane, and *n*-dodecane.

Effective collision diameters have been determined on the basis of simple kinetic-theory formulæ for mass diffusion. Such diameters confirm previous conclusions from viscosity data that on an average the flexible molecules are substantially crumpled at ordinary temperatures. Furthermore, in collisions with molecular hydrogen effective collision diameters of *flexible* hydrocarbons are larger than for collisions with gases such as nitrogen, oxygen, and argon. This behaviour may be related to other "hydrogen effects" due to facilitating internal-energy $\rightleftharpoons$ translational-energy transfers.

It has been shown (McCoubrey, McCrea, and Ubbelohde, *J.*, 1951, 1961; Cummings, McCoubrey, and Ubbelohde, *J.*, 1952, 2725) that viscosity data for a wide range of hydrocarbons of low molecular weight indicate substantial crumpling of the flexible molecules in the vapour phase at ordinary temperatures. By use of the viscosity and the temperature coefficient of viscosity of the vapours as parameters related to molecular configuration, significant trends as a function of molecular structure have been found. The present work was undertaken to compare any observable trends in the collision cross-sections for mass transfer with trends apparent in momentum transfer. Particular attention has been paid to hydrogen–hydrocarbon collisons in view of the special rôle of hydrogen in certain hydrocarbon reactions (cf. Small and Ubbelohde, *J.*, 1950, 723; *J. Appl. Chem.*, 1953, **3**, 193).

Experimental

Materials.—For preparations of *n*-hexane, methyl*cyclo*pentane, and 2 : 2 : 4-trimethylpentane see McCoubrey, McCrea, and Ubbelohde (*loc. cit.*), and for those of 2 : 3-dimethylbutane and *cyclo*hexane see Cummings, McCoubrey, and Ubbelohde (*loc. cit.*).

n-Octane and *n*-decane (B.D.H.) were washed with concentrated sulphuric acid until tests with bromine in carbon tetrachloride and with potassium permanganate in sodium carbonate solution indicated complete absence of unsaturated material. After being washed with sodium carbonate solution and with distilled water, and dried ($CaCl_2$), the compounds were stored over sodium wire, refluxed, and then distilled over sodium. Samples were finally fractionated through a 6″-column packed with phosphor-bronze gauze at reflux ratios of greater than 20 : 1 (design kindly provided by Imperial Chemical Industries Limited).

n-Dodecane was prepared from *n*-hexyl bromide (B.D.H.) by the Wurtz reaction (Mair, *J. Res. Nat. Bur. Stand.*, 1932, **9**, 457), and was purified as above.

Urea adducts of *n*-decane and *n*-dodecane were made (Zimmerschield, Dinerstein, Weitkamp, and Marschner, *Ind. Eng. Chem.*, 1950, **42**, 1300). The hydrocarbon regenerated from them had, after purification, the same physical properties as the original sample.

2 : 3 : 3-Trimethylheptane was kindly suppled by Shell Petroleum Co. (Thornton Research Laboratory).

Constants are recorded in the Table (boiling range ±0·1°).

Compound	B. p./mm.	n_D^{20}	*d* (temp.)
n-Hexane	68·3°/760	1·3743	0·6593 (20°)
2 : 3-Dimethylbutane	57·8°/761	1·3750	0·6653 (12·0°)
*cyclo*Hexane	80·7°/760	1·4262	0·7831 (15·0°)
Methyl*cyclo*pentane	71·5°/760	1·4095	0·7486 (20·0°)
n-Octane	125·0°/750	1·3974	0·6992 (24·2°)
2 : 2 : 4-Trimethylpentane	98·3°/742	1·3914	0·6885 (24·2°)
n-Decane	174·5°/766	1·4116	0·7269 (24·3°)
2 : 3 : 3-Trimethylheptane	160·1°/760	1·4207	0·756 (18·0°)
n-Dodecane	216·1°/760	1·4218	0·7463 (24·2°)

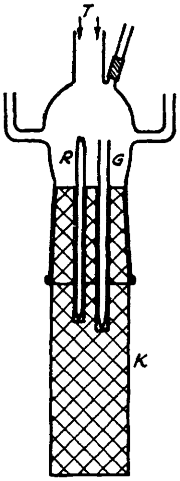
Carrier Gases.—The carrier gases—hydrogen, nitrogen, oxygen, and argon—were supplied by British Oxygen Co.

Apparatus and Technique.—The Stefan method was used for the determination of the mass-diffusion coefficients of the selected gas–vapour systems (*Ann. Physik*, 1882, **17**, 550; 1890, **61**, 725). Preliminary investigation of the Stefan technique was carried out with the system methyl*cyclo*pentane–air, and may be summarized as follows :

(*a*) Careful comparisons (see Fig. 1) were made of surface temperatures of the liquids in rhodium-plated silver and glass (soda and Pyrex) diffusion tubes. Glass was much easier to use because the liquid content could be read directly with a travelling microscope, whereas a silver tube would have to be weighed at intervals. If any serious temperature difference is set up near the surface of the liquid owing to evaporation, this would vitiate the calculations of diffusion coefficients. At comparable rates of evaporation any temperature gradient would be much reduced by the high conductivity of the silver walls. However, differential thermocouple readings between the surface and the bulk of the liquid verified that at the evaporation rates used differences did not exceed 0·05° in either glass or silver tubes. Glass was therefore used for most of the experiments.

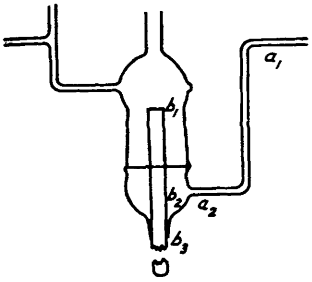
Temperature effects at the liquid–vapour interface have also been studied by control of the height of the gas–vapour diffusion column, and the flow rate of the carrier gas (cf. Trautz and Ludwig, *Ann. Physik*, **1930**, **7**, 887; Schwertz and Brow, *J. Chem. Phys.*, **1951**, **19**, 640).

FIG. 1.



T, Thermocouple leads.
R, Rhodium-plated silver diffusion tube.
G, Glass diffusion tube.
K, Solid brass cylinder.

FIG. 2.



(*b*) The diffusion coefficient D was found to be independent of the flow rate of the carrier gas, within the limits of experimental error, for flow rates in the range 100—400 c.c./min. (cf. Trautz and Muller, *Ann. Physik*, 1935, **22**, 353; Schwertz and Brow, *loc. cit.*; Kimpton and Wall, *J. Phys. Chem.*, 1952, **56**, 715).

(*c*) D was also independent, within the limits of experimental error, of the height of the gas–vapour diffusion column within the range 8—20 cm.

The Pyrex diffusion cell (see Fig. 2) could be opened by means of the cone and socket (B40) and was equipped with suitable side-arms for the passage of the carrier gas. For measurements of diffusion coefficients below 40°, the lower end of the diffusion chamber was drawn down to a narrow sleeve b_3; the glass diffusion tube b_1—b_2 fitted closely into this sleeve and was waxed into position. For measurements at higher temperatures the sleeve was replaced by a Pyrex tube extending to the bottom, and the glass diffusion tube fitted closely into it.

The diffusion cell and a Pyrex spiral preheater (350-cm. path) were immersed in a liquid bath, electrically controlled to $\pm 0{\cdot}1°$, the temperature being recorded by means of a 3-junction copper–constantan thermocouple. After passing through calcium chloride and silica gel tubes and the preheater, the carrier gas entered the diffusion chamber *via* a_1—a_2 at a point well below the mouth of the diffusion tube. A lead was taken from a side-arm to a manometer.

After the carrier gas had flowed for at least 45 min. to provide equilibrium, the height of the gas–vapour diffusion column was recorded at regular time intervals by means of a Pye cathetometer ($\pm$0·0005 cm.). The total pressure in the system and the thermostat temperature were read frequently.

The diffusion coefficient (cm.²/sec.), corrected to standard pressure, was calculated by using the equation

$$D_{760} = \frac{(h_2^2 - h_1^2)d_e P}{2(t_2 - t_1)d_s \times 760 \ln P/(P - Ps)}$$

where h_1 is the height of the gas–vapour diffusion column at time t_1, h_2 that time t_2, d_e is the liquid density (g./ml.) at the temperature of experiment, d_s that of the saturated vapour, P_s is the saturation vapour pressure (cm.) at the temperature of the experiment, and P is the average total pressure (cm.) in the diffusion chamber for the duration of an experiment.

The requisite vapour-pressure data were obtained from Nat. Bur. Stand., Circular C 461, 1947, and Thodos (*Ind. Eng. Chem.*, 1950, **42**, 1514) for all the hydrocarbons with the exception of 2 : 3 : 3-trimethylheptane. For this b. p.s were determined at pressures from 9 to 11 cm., a shielded thermometer being used and the usual precautions observed to ensure thermodynamic equilibrium. The vapour pressures required were obtained by interpolation.

TABLE 1.

Compound	Carrier gas	Temp. (K)	D_{760} (cm.²/sec.)	Precision of D ($\pm$) (%)	$2\sigma_{12}$
n-Hexane	H_2	288·7°	0·290	0·7	9·46
	N_2	288·6	0·0757	0·5	10·23
	O_2	288·6	0·0753	0·3	10·01
	A	288·6	0·0663	0·9	10·25
2 : 3-Dimethylbutane	H_2	288·8	0·301	1·0	9·29
	N_2	288·7	0·0751	1·3	10·28
	O_2	288·4	0·0753	0·3	10·00
	A	288·9	0·0657	1·1	10·30
*cyclo*Hexane	H_2	288·5	0·319	0·6	9·05
	N_2	288·6	0·0760	1·0	10·22
	O_2	288·6	0·0744	0·8	10·08
	A	288·7	0·0719	1·5	9·87
Methyl*cyclo*pentane	H_2	288·5	0·318	1·9	9·03
	N_2	285·9	0·0758	2·5	10·16
	O_2	287·1	0·0742	2·5	10·06
	A	288·6	0·0731	1·0	9·78
n-Octane	H_2	302·8	0·271	0·02	10·13
	N_2	303·0	0·0710	1·5	10·78
	O_2	303·1	0·0705	1·8	10·54
	A	303·0	0·0642	1·9	10·59
2 : 2 : 4-Trimethylpentane...	H_2	303·0	0·288	1·0	9·83
	N_2	"	0·0705	0·7	10·82
	O_2	"	0·0688	0·7	10·67
	A	"	0·0618	1·3	10·80
n-Decane	H_2	364·1	0·306	1·3	10·94
	N_2	363·6	0·0841	2·0	11·25
2 : 3 : 3-Trimethylheptane	H_2	363·9	0·270	1·6	11·64
	N_2	363·8	0·0684	0·8	12·48
n-Dodecane	H_2	399·6	0·308	1·8	11·68
	N_2	399·4	0·0813	2·0	12·20

Results are recorded in Table 1. The precision is governed by the rate of loss of vapour from the diffusion tube, which is, in turn governed principally by the height h of the gas–vapour diffusion column and the saturation vapour pressure of the hydrocarbon at the temperature of the experiment. As a result of the control of these variables, the precision achieved was in most cases better than $\pm$1·5%.

DISCUSSION

In the present state of the kinetic theory of gases, as applied to molecules of complicated structure, the " collision diameters " are best regarded primarily as parameters calculated in specified ways. From trends of behaviour of these parameters in systematic variations of molecular structure comparative information can be obtained about the effective behaviour of the molecules in collisions involving transfer of mass, momentum, or energy. But the numerical figures quoted cannot as yet be compared for exactness with numerical results obtained, for example, from optical or infra-red measurements on molecular structure.

The collision cross-sections σ_{12} for mass transfer have been calculated for the selected systems from the simple kinetic theory formula (Chapman and Cowling, " Mathematical Theory of Non-Uniform Gases," Cambridge Univ. Press, 1939) :

$$[D_{12}]_1 = \frac{3}{8n\sigma_{12}^2}\left\{\frac{kT\,(m_1 + m_2)}{2\pi m_1 m_2}\right\}^{\frac{1}{2}}$$

where the symbols have the usual significance. The mass diffusion collision diameters (σ_2) for the hydrocarbon molecules recorded in Table 2 have been calculated from these by using the relation $\sigma_{12} = \frac{1}{2}(\sigma_1 + \sigma_2)$ and literature values of σ_1 for the carrier gas molecules (Chapman and Cowling, *op. cit.*, p. 229).

General consideration of the σ_2 cross-sections thus evaluated indicates that the diameters for mass-transfer for the *n*- and the *iso*-compounds of the C_6 or C_8 series are approximately equal. This confirms the previous conclusions, from viscosity data, that *n*-paraffins behave in collisions as if they are substantially crumpled in the vapour phase even at ordinary temperatures. For C_{10} hydrocarbons the mass-diffusion diameters give further support to this conclusion.

More detailed consideration of the results within the series of isomeric C_6 hydrocarbons indicates that the effective diameters for collisions with nitrogen and oxygen are closely similar, within $\pm 1\%$. Experimental inaccuracy of $\pm 2\%$ in D can account for $\pm 1\%$ in σ_2. With argon, the cyclic molecules show markedly lower effective collision diameters. With hydrogen, the " hydrogen effect " previously suggested (McCoubrey and Ubbelohde, *Discuss. Faraday Soc.*, 1951, **10**, 94) is exhibited by all the series of compounds now studied. Mass-diffusion collision diameters of the more flexible hydrocarbons are systematically higher with hydrogen than with nitrogen or oxygen. The less flexible hydrocarbons do not show this effect.

TABLE 2. *Apparent collision diameters of hydrocarbons* (σ_2).

Carrier gas: Compound	H_2 ($\sigma_1 = 2{\cdot}73$)	N_2 ($\sigma_1 = 3{\cdot}75$)	$\Delta\{\sigma_{H_2} - \sigma_{N_2}\}$	O_2 ($\sigma_1 = 3{\cdot}62$)	A ($\sigma_1 = 3{\cdot}66$)
C_2 *series.*					
Ethylene [a]	4·80	3·67	+1·13	—	—
Ethane [b]	4·47	4·49	−0·02	—	—
C_6 *series.*					
n-Hexane	6·73	6·48	+0·25	6·39	6·59
2 : 3-Dimethylbutane	6·56	6·53	+0·03	6·38	6·64
*cyclo*Hexane	6·32	6·47	−0·15	6·46	6·21
Methyl*cyclo*pentane	6·30	6·41	−0·11	6·47	6·12
Benzene [a]	5·74	5·70	+0·04	—	—
C_8 *series.*					
n-Octane	7·40	7·03	+0·37	6·92	6·93
2 : 2 : 4-Trimethylpentane	7·10	7·07	+0·03	7·05	7·14
C_{10} *series.*					
n-Decane	8·21	7·50	+0·71	—	—
2 : 3 : 3-Trimethylheptane	8·91	8·73	+0·18	—	—
C_{12} *series.*					
n-Dodecane	8·95	8·45	+0·50	—	—
Dibutyl phthalate [c]	9·40	8·94	+0·46	—	—

[a] Trautz and Muller, *Ann. Physik.*, 1935, **22**, 350, 371. [b] Boyd, Stein, Steingrimsson, and Rumpel, *J. Chem. Phys.*, 1951, **19**, 548. [c] Birks and Bradley, *Proc. Roy. Soc.*, 1949, *A*, **198**, 226.

Theoretically, the diffusion coefficient is decreased, and hence the effective collision diameter is increased, by the occurrence of inelastic collisions which transfer of energy from translational to other degrees of freedom (Chapman and Cowling, *loc. cit.*; Pidduck, *Proc. Roy. Soc.*, 1922, *A*, **101**, 101). This explains for example the hydrogen effect with ethylene, compared with ethane (Table 2). Ultrasonic relaxation experiments have verified this exceptional efficiency of hydrogen in transferring internal energy to ethylene (Richards, *J. Chem. Phys.*, 1936, **4**, 561).

One factor in accounting for the hydrogen effect now observed is the low mass of hydrogen, which favours transfer of vibrational energy in collisions (Schwartz, Slawsky, and Herzfeld, *J. Chem. Phys.*, 1952, **20**, 1591), but for molecules of comparable mass a further factor is the molecular flexibility. High flexibility enhances any hydrogen effect markedly. An interpretation of chemical reactions susceptible to hydrogen collisions, such as the thermal decomposition of complex organic molecules, and the marginal oxidation of hydrocarbons (Small and Ubbelohde, *loc. cit.*) is that hydrogen facilitates transfers of internal energy, particularly of vibrational energy. It may be significant for hydrocarbon oxidation that with paraffins this ease of transfer is linked with molecular flexibility.

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