

*Collision Parameters of C₆—C₉ Hydrocarbons in the Vapour Phase :
The Hydrogen Effect.*

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With nitrogen and hydrogen as carrier gases mass-diffusion coefficients have been measured for the compounds hexa-1 : 5-diene, 2 : 3-dimethylbuta-1 : 3-diene, 2 : 3-dimethylbut-2-ene, *n*-heptane, and *n*-nonane. These supply missing information in the gas-kinetic parameters for the C₆—C₉ range.

Results extend previous evidence that on the average the flexible hydrocarbons are substantially crumpled at normal temperatures in the vapour phase. Differences in effective hydrocarbon-collision diameters for hydrogen-hydrocarbon and nitrogen-hydrocarbon collisions (the "hydrogen effect") are discussed with reference to the influence of molecular flexibility, inelastic collisions, and the nature of the intermolecular potential. A marked hydrogen effect is found for the more flexible hydrocarbons.

NUMERICAL trends as a function of molecular structure in collision parameters deduced from viscosity data (Cummings, McCoubrey, and Ubbelohde, *J.*, 1952, 2725) indicated substantial crumpling of flexible hydrocarbons in the vapour phase at normal temperatures. Collision parameters deduced for mass-diffusion (Cummings and Ubbelohde, *J.*, 1953, 3751) in nitrogen-hydrocarbon systems confirmed this and showed the general trends apparent in momentum-transfer parameters. Hydrocarbon "diameters" in collisions with hydrogen have been found to be greater than for the corresponding collisions with nitrogen when the hydrocarbon molecule is flexible. This effect was tentatively attributed to the occurrence of inelastic collisions. The present research has been undertaken in order to extend the previous findings to fresh examples in the C₆—C₉ range of hydrocarbons.

EXPERIMENTAL

Materials.—The preparation and purification of hexa-1 : 5-diene, 2 : 3-dimethylbuta-1 : 3-diene, and 2 : 3-dimethylbut-2-ene have been described by Cummings, McCoubrey, and Ubbelohde (*loc. cit.*). The properties of the purified samples will be given elsewhere (Cummings and McLaughlin, in the press). Samples of 99.9 mole-% *n*-heptane (b. p. 98.4°/760 mm., n_D^{20} 1.3876) and *n*-nonane (b. p. 150.8°/760 mm., n_D^{20} 1.4055) were gifts from the Anglo-Iranian Oil Co., to whom thanks are offered for their support of this work.

Apparatus and Technique.—The apparatus and technique for measuring mass diffusion were as described previously (Cummings and Ubbelohde, *loc. cit.*). Special precautions were taken in the handling of the unsaturated compounds (Howard, Mears, Fookson, Pomerantz, and Brooks, *J. Res. Nat. Bur. Stand.*, 1947, 38, 365). The diffusion coefficient, D_{12} (cm.²/sec.), corrected to standard pressure was calculated from the equation :

$$D_{12}^{760} = \frac{(h_2^2 - h_1^2)d_e P}{2(t_2 - t_1)d_s \times 760 \ln [P/(P - P_s)]} \quad \dots \quad (1)$$

which assumes perfect gas laws. h_1 is the height of the gas-vapour diffusion column at time t_1 , and h_2 that at time t_2 . d_e is the density of the liquid (g./ml.) d_s that of the saturated vapour, and P_s the saturation vapour pressure (cm.) at the temperature of experiment. The average total pressure (cm.) for the duration of the experiment is denoted by P .

Vapour-pressure data are available for *n*-heptane (Nat. Bur. Stand., Circular C461, 1947) and *n*-nonane (Rossini, Forziati, and Norris, *J. Res. Nat. Bur. Stand.*, 1949, 43, 555). Measurement of the vapour pressures of the unsaturated hydrocarbons are reported elsewhere (Cummings and McLaughlin, in the press).

During the approximate three-hour periods between successive observations the average pressure and temperature fluctuations did not exceed ± 0.2 mm. and $\pm 0.05^\circ$ respectively. Diffusion coefficients calculated from equation 1 are recorded in Table 1, together with standard deviations.

TABLE 1.

Compound	Carrier gas	Temp. (°K)	D_{12}^{750} (cm. ² /sec.)	No. of observations	Precision of D_{12} (±)
Hexa-1 : 5-diene	H ₂	288.1	0.298	15	0.005
	N ₂	288.1	0.0772	12	0.0015
2 : 3-Dimethylbuta-1 : 3-diene	H ₂	288.1	0.312	9	0.005
	N ₂	288.1	0.0748	6	0.0025
2 : 3-Dimethylbut-2-ene	H ₂	288.1	0.296	8	0.006
	N ₂	288.3	0.0705	8	0.0013
<i>n</i> -Heptane	H ₂	303.0	0.286	12	0.004
	N ₂	303.0	0.0743	8	0.0012
<i>n</i> -Nonane	H ₂	339.8	0.284	7	0.002
	N ₂	339.8	0.0737	8	0.0003

DISCUSSION

The heteromolecular collision cross-section σ_{12} can be defined in various ways depending on the form of the assumed intermolecular potential. Earlier results have been interpreted wholly on the basis of the rigid-sphere model. In this analysis (Chapman and Cowling, "Mathematical Theory of Non-Uniform Gases," Cambridge Univ. Press, 1939) the molecules are treated as hard rigid elastic spheres and the cross-section σ_{12} is defined by

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

where $(D_{12})_1$ is the first approximation for the diffusion coefficient, and the other symbols have their usual significance. For the more realistic Lennard-Jones potential of the form

$$V(r) = 4\epsilon_{12}[(\sigma_{12}/r)^{12} - (\sigma_{12}/r)^6]$$

which takes account of the fact that molecules have superimposed attractive and repulsive force fields, the cross-section σ_{12} is defined by

$$(D_{12})_1 = \frac{3}{16n\sigma_{12}^2} \left\{ \frac{kT(m_1 + m_2)}{2\pi m_1 m_2} \right\}^{\frac{1}{2}} \frac{1}{W^1(1; kT/\epsilon_{12})} \cdot \cdot \cdot \cdot \cdot \cdot \quad (3)$$

where $W^1(1; kT/\epsilon_{12})$, the collision integral, is a tabulated function (Hirschfelder, Bird, and Spotz, *J. Chem. Phys.*, 1948, **16**, 968) of kT/ϵ_{12} , the force constant for the heteromolecular interaction. Table 2 gives the values of the cross-sections evaluated on the

TABLE 2. Calculated cross-sections for hydrocarbons (σ_{22}) (mass transport) (Å).

Compound	Rigid-sphere model			12 : 6 Model		
	N ₂	H ₂	Δ	N ₂	H ₂	Δ
<i>n</i> -Hexane *	6.51	6.78	+0.27	5.72	6.82	+1.10
Hexa-1 : 5-diene	6.41	6.60	+0.19	5.38	6.18	+0.80
2 : 3-Dimethylbutane *	6.53	6.60	+0.07	6.13	6.65	+0.52
2 : 3-Dimethylbuta-1 : 3-diene	6.57	6.39	-0.18	6.23	6.50	+0.27
2 : 3-Dimethylbut-2-ene	6.87	6.63	-0.24	6.89	6.99	+0.10
<i>cyclo</i> Hexane *	6.58	6.30	-0.28	6.08	6.34	+0.26
<i>n</i> -Heptane †	6.88	7.15	+0.27	5.96	6.96	+1.0
<i>n</i> -Octane *	6.94	7.31	+0.37	6.34	7.27	+0.93
2 : 2 : 4-Trimethylpentane * †	7.02	7.05	+0.03	6.61	7.02	+0.51
<i>n</i> -Nonane	7.74	8.07	+0.33	7.64	8.44	+0.80

* Values included in Table 2 from earlier work for convenience.

† ϵ/k for *n*-heptane and *isooctane* are derived from the empirical relation $\epsilon/k = 1.39T_b$ (Hirschfelder, Bird, and Spotz, *Trans. Amer. Soc. Mech. Eng.*, 1949, **71**, 921).

basis of equations 2 and 3. The requisite values of kT/ϵ were taken from viscosity data for the pure components (Cummings, McCoubrey, and Ubbelohde, *loc. cit.*; Hirschfelder, Curtiss, and Bird, "The Molecular Theory of Gases and Liquids," Wiley & Sons, Inc., New York, 1954) and kT/ϵ_{12} and σ_{22} were evaluated by using the empirical relations:

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{\frac{1}{2}}$$

$$\sigma_{12} = \frac{1}{2}(\sigma_{11} + \sigma_{22})$$

where σ_{11} and σ_{22} are the cross-sections for the carrier gas and hydrocarbon respectively. Table 2 also contains cross-sections calculated from the results of Cummings and Ubbelohde (*loc. cit.*) on the basis of the Lennard-Jones 12 : 6 potential. Values quoted in the above paper have been corrected for a small pressure term as explained in a forthcoming note.

The quantity Δ in Table 2 is defined by :

$$\Delta = \sigma_{22}(\text{H}_2) - \sigma_{22}(\text{N}_2)$$

where $\sigma_{22}(\text{H}_2)$ is the cross-section for the hydrocarbon when in collision with hydrogen and $\sigma_{22}(\text{N}_2)$ that when in collision with nitrogen. The values of $\sigma_{11}(\text{H}_2)$ and $\sigma_{11}(\text{N}_2)$ are obtained from Johnston and McCloskey's viscosity results (*J. Phys. Chem.*, 1940, **44**, 1038). On the rigid-sphere model $\sigma_{11}(\text{N}_2)$ is 3.75 and $\sigma_{11}(\text{H}_2)$ is 2.73 Å, while on the Lennard-Jones 12 : 6 model $\sigma_{11}(\text{N}_2)$ is 3.68 and $\sigma_{11}(\text{H}_2)$ is 2.97 Å.

Crumpling of the Molecules.—Inspection of $\sigma_{22}(\text{N}_2)$ in Table 2 for the C₆ compounds on either of these gas-kinetic models shows a trend in cross-section with molecular flexibility. The most rigid molecule 2 : 3-dimethylbut-2-ene has the largest cross-section, and hexa-1 : 5-diene which is the most flexible has the smallest. The same trend was observed in momentum transfer cross-section (Cummings, McCoubrey, and Ubbelohde, *loc. cit.*). Justification for applying the kinetic theory approximations used here lies in the comparative character of the method adopted. The conclusions are based essentially on the observed variations in parameters defined in a specific manner for a range of related molecules. The use of the more realistic intermolecular potential (12 : 6) for definition of the parameters gives the same general trends as are observed with the simpler rigid-sphere model, but to an even more marked degree.

The Hydrogen Effect with Flexible Molecules.—Inspection of Table 2 shows that, whatever model is used, Δ has a finite positive value for flexible molecules, which is definitely larger than for relatively stiff molecules of similar mass. In contrasting hydrogen-hydrocarbon and nitrogen-hydrocarbon collision processes, three factors may be considered as possible causes for the differences found : (1) Quantum effects may be more important with hydrogen than with nitrogen. (2) Departure from spherical symmetry of the intermolecular potential in the colliding species may lead to differences between hydrogen and nitrogen collisions with hydrocarbons. (3) The rate of transfer, reversibly, from translational to internal energy in collision between hydrogen and the flexible hydrocarbons may be markedly greater than in collisions with nitrogen.

Quantum deviations in the transport properties of systems involving hydrogen in the temperature range considered are generally assumed to be negligible (cf. Mason and Rice, *J. Chem. Phys.*, 1954, **22**, 522). This is also borne out by simple De Broglie wave-length considerations.

The effect of non-spherical symmetry of the intermolecular potential on transport properties has not yet been calculated in detail. In the comparative method adopted, effects due to the non-spherical shape of the hydrocarbon molecules should cancel out when *differences* are calculated between $\sigma(\text{H}_2)$ and $\sigma(\text{N}_2)$.

Finally, the Bryan-Pidduck model (Chapman and Cowling, *op. cit.*; Pidduck, *Proc. Roy. Soc.*, 1922, *A*, **101**, 101) provides a means of estimating the influence of inelastic collisions on transport properties. This method of calculation shows that effective transfer of energy between internal and translational degrees of freedom leads to a decrease in diffusion coefficient and effectively increases the cross-section. Moreover, ultrasonic measurements support the view that molecular flexibility markedly enhances the probability of inelastic collisions (McGrath and Ubbelohde, in the press; McCoubrey, Parke, and Ubbelohde, *Proc. Roy. Soc.*, 1954, *A*, **223**, 155). It has been known for some time that hydrogen is peculiarly effective in leading to inelastic collisions. Thus theoretical (Schwartz, Slawsky, and Herzfeld, *J. Chem. Phys.*, 1952, **20**, 1591; Takayanagi, *Progr. Theor. Phys.*, 1952, **8**, 111) and experimental work (Richards, *J. Chem. Phys.*, 1936, **4**, 561) give direct support to the view that hydrogen is extremely efficient in transferring energy on collision. From a more chemical standpoint, the exceptional efficiency of hydrogen can also be inferred from its influence on the unimolecular decomposition of

ethers (Hinshelwood, "Kinetics of Chemical Change," Oxford Univ. Press, 1949) and on the gaseous oxidation of acetaldehyde and *n*-hexane (Small and Ubbelohde, *Nature*, 1951, **168**, 201; *J. Appl. Chem.*, 1953, **3**, 193). The new findings support the view that this exceptional efficiency of hydrogen is particularly marked in collision with flexible molecules.

It is of interest to consider how the "hydrogen effect" would vary in a homologous series, starting with comparatively inflexible molecules and proceeding to molecules of greater flexibility and molecular weight. So far as the accuracy of the present method permits, once a certain degree of flexibility has been attained an asymptotic state is reached. There appears to be no marked further rise in Δ with increasing chain length.

Since each collision is localised this is perhaps to be expected. Molecular flexibility merely smears quantum restrictions in the region immediately around the collision complex. Once these have attained approximately the classical values, no further effects are to be expected with still greater increase in chain length.

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