

LETTERS TO THE EDITORS

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Transfer of Internal Energy in Molecular Collisions of Flexible Hydrocarbons

A WELL-KNOWN problem in the physical chemistry of aliphatic hydrocarbons is to account for the marked dependence of reactivity on molecular structure, especially for reactions in the gas phase. For example, in oxidation of isomeric paraffins below about 300°, reactivity is greatest for the least-branched chain. Among the normal paraffins, the reactivity of homologues increases as the chain-length increases¹. Various explanations of this influence of molecular structure on chemical reactivity have been suggested. Marked polar influences or valency drifts of electrons are not likely to be significant in this class of molecules. Molecular structure is, however, likely to have a marked effect on the degree of coupling between vibrations in different parts of the molecule² and also on the degree of flexibility of the hydrocarbon³.

Gas kinetic studies have shown⁴ that even normal paraffins are extensively crumpled at ordinary temperatures, as a result of rotations about C—C single bonds. Molecular flexibility seems to be an important factor in facilitating transfer of internal energy in gaseous collisions. In mass diffusion, flexible hydrocarbons show "hydrogen-effects"⁵, and there is an enhanced transfer of internal energy on collision with molecular hydrogen. Again, from ultrasonic measurements on mixtures of ethylene with other gases⁶, paraffin hydrocarbons prove to be very efficient in transferring vibrational energy to the ethylene. These observations have been ascribed to "wrestling collisions" arising from the flexibility of these molecules.

We have now found a striking effect of molecular flexibility in the collision efficiency of hydrocarbons of the C₅ and C₆ groups, for transferring vibrational energy to ethylene. As the hydrocarbon molecule becomes stiffer, a marked increase is required in the number Z_{eff} of collisions with an ethylene molecule before the transfer of a quantum of vibrational energy 0 → 1 will take place to the ethylene.

At 298° K. the values of Z_{eff} are found to be approximately:

| Hydrocarbon | <i>n</i> -pentane | <i>iso</i> -pentane | <i>neo</i> -pentane | ethylene (self-collisions) | <i>cyclo</i> -pentane |
|------------------|-------------------|---------------------|---------------------|----------------------------|-----------------------|
| Z _{eff} | 50 | 60 | 120 | 2,500 | 3,300 |

| Hydrocarbon | <i>n</i> -hexane | <i>iso</i> hexane | <i>cyclo</i> hexane |
|------------------|------------------|-------------------|---------------------|
| Z _{eff} | 30 | 40 | 100 |

The marked contrast in collision efficiencies between *cyclopentane* and *cyclohexane* accords with previous suggestions about wrestling collisions. These are much more likely to blur vibrational quantum levels and thus to facilitate the transfer translational → internal energy when a flexible molecule is one of the collision partners. It is noteworthy that collisions with the stiff *cyclopentane* molecule are even less

efficient for promoting vibrational energy transfer than self-collisions between two ethylene molecules.

Since chemical reactions of the paraffins in the gas phase show evidence of involving the 'chain transfer' of energy⁷, it becomes understandable that factors such as molecular flexibility which control energy transfer can also control relative reactivity, in the absence of more powerful influences.

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¹ Ubbelohde, A. R., *Proc. Roy. Soc., A*, **152**, 361 (1935). Cullis, C. F., and Himshelwood, C. N., *Disc. Farad. Soc.*, No. 2, 117 (1947).

² Ubbelohde, A. R., *Rev. Inst. franç. du Pétrole et Ann. Combustibles liquides*, **4**, 488 (1949).

³ Ubbelohde, A. R., and McCoubrey, J. C., *Disc. Farad. Soc. (Hydrocarbons)*, No. 10, 94 (1951).

⁴ McCoubrey, J. C., McCrea, J. N., and Ubbelohde, A. R., *J. Chem. Soc.*, 1961 (1951). Cummings, G. A. McD., McCoubrey, J. C., and Ubbelohde, A. R., *J. Chem. Soc.*, 2725 (1952). McCoubrey, J. C., and Ubbelohde, A. R., *Quart. Rev.*, No. 4, 356 (1951).

⁵ Cummings, G. A. McD., and Ubbelohde, A. R., *J. Chem. Soc.*, 3751 (1953).

⁶ McCoubrey, J. C., Parke, J. B., and Ubbelohde, A. R., *Proc. Roy. Soc. (in the press)*.

⁷ Small, N. J. H., and Ubbelohde, A. R., *J. App. Chem.*, **3**, 193 (1953)

A Two-Crystal Gamma-Ray Scintillation Spectrometer

THE scintillation spectrometer¹ using a sodium iodide crystal (thallium-activated) identifies the incident gamma-ray energy with the response to the photo-electric, Compton and (when energetically possible) with the pair-production processes within the crystal. In sodium iodide, the photo-electric cross-section is predominant below about 0.2 MeV. and the pair-production process becomes appreciable above about 2.5 MeV. In the energy-range 0.2–2.5 MeV., the photo-electric and Compton processes are in competition. Thus, the recorded spectrum in this important range is complicated by the two-fold response of the spectrometer to each gamma-ray line.

Several methods of selection in favour of one of the two processes are available which simplify the interpretation of the records when a source emitting several gamma-ray lines has to be analysed. Use of a sodium iodide crystal of large dimensions enhances the photo-electric or 'total' energy peak at the expense of the Compton energy continuum, due to the capture of the scattered quanta. Substitution of anthracene, essentially a Compton absorber, for the sodium iodide crystal removes the photo-electric peaks; the energy of the gamma-ray can then be roughly estimated from the poorly defined edge of the Compton continuum. A two-crystal coincidence spectrometer has been reported by Hofstadter and McIntyre². In this method the energy absorbed by those Compton encounters which scatter the incident rays through a defined angle is measured. More recently, a method has been described by Albert³ in which the quanta scattered by a small sodium iodide crystal are detected in a surrounding mass of sodium iodide, and the pulses due to the corresponding Compton electrons in the crystal are cancelled by anticoincidence.

In the two-crystal spectrometer described here the gamma-ray source is exposed simultaneously to sodium iodide and anthracene scintillation counters. The Compton continua from the two crystals are