849. *Charge-transfer Spectra involving Saturated Hydrocarbons.*

By D. F. Evans.

The strong ultraviolet absorption of iodine dissolved in a number of saturated hydrocarbons has been measured, and is discussed in connection with recent theories of charge-transfer spectra. A distinct band around 2400 Å is observed (at room temperature or −127°) with hydrocarbons containing a *cyclo*hexane ring, thus indicating that a *cyclo*hexane ring has appreciably greater donor properties than an open-chain saturated hydrocarbon or a *cyclo*pentane ring. The ultraviolet spectrum of tetranitromethane in 2 : 2 : 4-trimethylpentane or *cyclo*hexane shows considerable long-wavelength absorption not found in the vapour phase. This is attributed to charge-transfer transitions, and, in agreement with this, no comparable effect is observed with nitromethane.

Evidence has been growing recently that, in the ultraviolet region, saturated hydrocarbons are not always the inert spectroscopic solvents usually believed. Hastings, Franklin, Schiller, and Matsen[1] originally showed that iodine dissolved in saturated hydrocarbons such as *n*-heptane and *cyclo*hexane has strong absorption below 2600 Å which varies appreciably with the hydrocarbon studied. They assumed that the spectrum in *n*-hexane was characteristic of iodine itself and, by subtracting this from the other measured spectra, obtained what were regarded as charge-transfer spectra of very weak saturated hydrocarbon–iodine complexes, analogous to the well-established aromatic hydrocarbon–iodine complexes.

However, it was shown[2] that this assumption is almost certainly incorrect, since the strong absorption is not found with iodine in the gas phase or dissolved in fully fluorinated solvents (down to 2100 Å), and is present to a much smaller extent with iodine in chloroform. These results, together with measurements in mixed *n*-heptane–perfluoroheptane solutions, made it very unlikely that a solvent shift of the strong *N–V* transition (with a maximum at 1750 Å) is involved, and it was concluded that the greater part of the absorption (even with *n*-hexane) is due to a charge-transfer transition. According to a recent accurate determination[3] the ionisation potential of chloroform[3] (11·42 ± 0·03 v) is considerably greater than that of *n*-hexane[4] (10·43 v), which agrees with the above interpretation of the iodine spectra. Bromine behaves similarly to iodine.[5] Oxygen dissolved in saturated hydrocarbons absorbs appreciably below about 2500 Å, and this has again been attributed to charge-transfer transitions.[2, 6, 7]

There is, however, some uncertainty as to the species responsible for these transitions. By analogy with the large number of well-defined molecular complexes of the donor–acceptor type, it is possible that very weak complexes are involved. Alternatively, it was suggested[2] that a charge-transfer transition might occur during the collision of an iodine molecule with a hydrocarbon molecule, in the absence of any complex formation; this idea was extended by Orgel and Mulliken,[8] who gave theoretical reasons for supposing that a charge-transfer transition can occur between an iodine (or other acceptor) molecule and a hydrocarbon molecule which are merely in contact (" contact charge-transfer spectra "). The absence of any independent evidence for complex formation in these solutions[9,10] agrees with this interpretation.

[1] Hastings, Franklin, Schiller, and Matsen, *J. Amer. Chem. Soc.*, 1953, **75**, 2900.
[2] Evans, *J. Chem. Phys.*, 1955, **23**, 1424.
[3] Watanabe, *ibid.*, 1957, **26**, 542.
[4] Honig, *ibid.*, 1948, **16**, 105.
[5] Evans, *ibid.*, 1955, **23**, 1426.
[6] Evans, *J.*, 1953, 345.
[7] Munck and Scott, *Nature*, 1956, **177**, 587.
[8] Mulliken, *Rec. Trav. chim.*, 1956, **75**, 845.
[9] Kortüm and Vogel, *Z. Electrochem.*, 1955, **59**, 16.
[10] Jepson and Rowlinson, *J.*, 1956, 1278.

Accordingly, further measurements on the absorption spectrum of iodine in saturated hydrocarbons have been made, at both room and low temperatures. Apart from the usual solvent shift due to changes in the refractive index of the solution, and also a possible sharpening of the bands, little change would be expected in contact charge-transfer spectra on cooling to low temperatures. The interaction of tetranitromethane, another acceptor molecule, with *cyclo*hexane and 2 : 2 : 4-trimethylpentane has also been studied.

EXPERIMENTAL

Materials.—For low-temperature measurements on iodine solutions the saturated hydrocarbons should be as free as possible from impurities such as aromatic compounds and olefins which form complexes with iodine, although the presence of *small* amounts of other saturated hydrocarbons is not objectionable. Commercial pure samples of the hydrocarbons were further purified, either by repeated shaking with fuming sulphuric acid, followed by washing, drying, and fractional distillation, or by passing them through a column of freshly baked silica gel. These procedures gave, for any particular hydrocarbon, products with almost identical absorptions in the region 2100—2500 Å. This absorption is largely, though not entirely, due to the dissolved atmospheric oxygen (cf. Evans [6] and Munck and Scott [7]). *cis*- and *trans*-Decalin (stated purity 99·9%) were further purified with silica gel. In addition, a commercial sample of decalin was treated with both fuming sulphuric acid and silica gel, and analysed by gas chromatography (67% *trans*, 33% *cis*). Tetranitromethane was shaken with dilute alkali, washed, dried, and fractionally distilled under reduced pressure. Nitromethane was dried and fractionally distilled.

Measurements.—A Unicam S.P. 500 spectrophotometer was used. The low-temperature cell is described elsewhere.[11] Solutions were deoxygenated with oxygen-free nitrogen, and corrections applied for the contraction of the solvent on cooling.

The spectra of gaseous tetranitromethane and nitromethane were obtained by placing a drop of the liquid in a 1 cm. stoppered cell contained in a thermostatted cell holder. Equilibrium was attained in 1—2 min., and the concentration of vapour obtained from vapour-pressure data.

RESULTS AND DISCUSSION

Iodine Solutions.—Low-temperature studies of iodine dissolved in saturated hydrocarbons are complicated by the possibility of iodine's crystallising from the solutions. Norman and Porter [12] claimed that stable yellow solutions could be obtained at liquid-nitrogen temperatures with concentrations of iodine as high as 10^{-3}M; the yellow colour was tentatively attributed to complex formation between the saturated hydrocarbon (*iso*pentane and methyl*cyclo*hexane) and iodine. Sowden and Davidson,[13] however, were able to obtain clear solutions only at much lower concentrations of iodine (*ca.* 10^{-4}M) and similar results were obtained in the present work (cf. also Ham [14]). It therefore seems likely that Norman and Porter's solvents were appreciably impure. The yellow colour of the very dilute solutions of iodine was attributed by Sowden and Davidson to minute amounts of complex-forming impurities such as benzene, and also to crystallisation. Alternatively, colloidal solutions may be formed. The sudden formation of the yellow colour on cooling the solutions below a certain temperature, and its non-disappearance on heating to an appreciably higher temperature (at which an initially violet solution remains unchanged) support this interpretation. In any case, it is very unlikely that the colour is due to complex formation between the saturated hydrocarbon and the iodine.

Fortunately, our iodine solutions were stable when cooled to about −130° and, as expected, there was virtually no shift of the 5200 Å visible band. The results obtained in the ultraviolet region for iodine dissolved in methyl*cyclo*hexane, methyl*cyclo*pentane, and 2-methylpentane are shown in Fig. 1. The most marked feature is the appearance of a well-defined shoulder around 2400 Å for methyl*cyclo*hexane at −127°, which can just be detected at room temperature with methyl*cyclo*hexane (and also *cyclo*hexane [1]). Since it

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[11] Evans, *J.*, 1957, 4013.

[12] Norman and Porter, *Proc. Roy. Soc.*, 1955, *A*, **230**, 399.

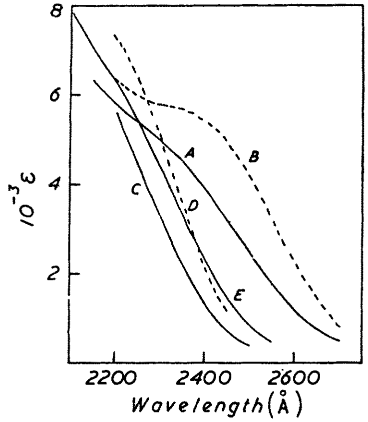
[13] Sowden and Davidson, *J. Amer. Chem. Soc.*, 1956, **78**, 1291.

[14] Ham, *ibid.*, 1954, **76**, 3875.

therefore seemed that a *cyclo*hexane ring had considerably greater donor properties than an open-chain saturated hydrocarbon or *cyclo*pentane ring, the absorption spectrum of iodine dissolved in *cis*- and *trans*-decalin was measured at room temperature (Fig. 2). The effect is even more marked, especially with *cis*-decalin. Although no new band can be detected down to 2200 Å for iodine in 2-methylpentane, one may be present at shorter wavelengths. There is an appreciable red shift of the absorption tail in this case, but the possibility that this is due to a " solvent " shift cannot be excluded.

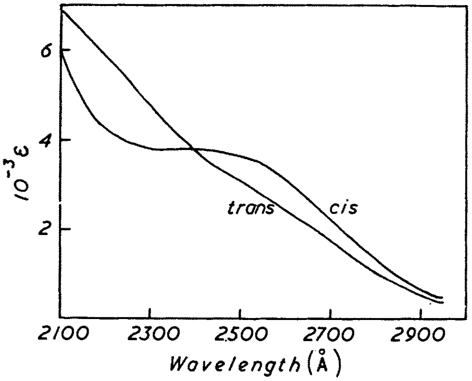
In considering possible explanations for the anomalous behaviour of the *cyclo*hexane ring, it is significant that the ionisation potential of *cyclo*hexane[3] (9·88 ± 0·02 v) is considerably smaller than those of typical open-chain hydrocarbons (*n*-hexane,[4] 10·43 v). Hastings, Franklin, Schiller, and Matsen[1] and McConnell, Ham, and Platt[15] showed that, as expected theoretically, there is a good correlation between the ionisation potential of a donor molecule and the wavelength of the corresponding charge-transfer band with iodine.

FIG. 1. *Absorption spectra of iodine in hydrocarbon solution.*



A, Methyl*cyclo*hexane at *ca.* 22°; *B*, methyl*cyclo*hexane at −127°; *C*, 2-methylpentane at *ca.* 22°; *D*, 2-methylpentane at −127°; *E*, methyl*cyclo*pentane at *ca.* 22°.

FIG. 2. *Absorption spectra of iodine in* cis- *and* trans-*decalin.*



Steric factors may also play a part, since the shape of a *cyclo*hexane ring will differ appreciably from that of an open-chain hydrocarbon.

The above results are of interest in connection with an effect observed by Ham[14] (during an extensive study of the absorption spectra of iodine complexes at low temperatures), that the charge-transfer bands of certain aromatic compound–iodine complexes showed a very large red shift on cooling to low temperatures in the presence of methyl*cyclo*hexane (but not 3-methylpentane or *iso*pentane). The shift was apparently due to the appearance of a distinct new band, tentatively attributed to a complex solvated by a methyl*cyclo*hexane molecule.

Freed and Sancier[16] observed a strong charge-transfer peak at 2400 Å for iodine in *cyclo*propane, and pointed out that this is not surprising in view of the similarity in chemical and physical properties between *cyclo*propane and olefins.[17]

As regards the original question of complex formation *versus* " contact charge-transfer spectra," although no definite conclusions can be drawn from our results it seems most likely that while a charge-transfer transition can result from two molecules merely in contact, certain configurations will be more stable thermodynamically than others, and

[15] Ham, Platt, and McConnell, *J. Chem. Phys.*, 1951, **19**, 1301.
[16] Freed and Sancier, *J. Amer. Chem. Soc.*, 1952, **74**, 1273.
[17] " Chemistry of Carbon Compounds," ed. Rodd, Elsevier, 1953, p. 27.

these will be increasingly favoured at lower temperatures. Some such stable configuration is presumably responsible for the new bands with *cyclo*hexane-type solvents. The residual absorption down to about 2100 Å, and most of the absorption with open-chain hydrocarbons, is probably largely due to contact charge-transfer spectra from random non-specific iodine–hydrocarbon configurations.

Charge-transfer Spectra with Tetranitromethane.—Charge-transfer spectra involving saturated hydrocarbons should clearly not be restricted to iodine, bromine, and oxygen. Unfortunately the great majority of other electron-accepting molecules show very strong absorption below about 2700 Å which would tend to obscure any charge-transfer band. However tetranitromethane, which gives charge-transfer spectra extending into the visible region with aromatic and olefinic molecules,[18] does not absorb very strongly above 2400 Å, and accordingly its spectrum was measured in the vapour phase and in *iso*octane and *cyclo*hexane solution. Both tetranitromethane and nitromethane have a very weak absorption maximum in the vapour phase at 2750 Å,[19, 20] which indicates that there is little interaction between the nitro-groups in the former. (This spectral similarity also extends to shorter wavelengths.) The spectrum of nitromethane was therefore measured under similar conditions for comparison, since although any solvent shift should be similar to that with tetranitromethane, no charge-transfer band would be expected.

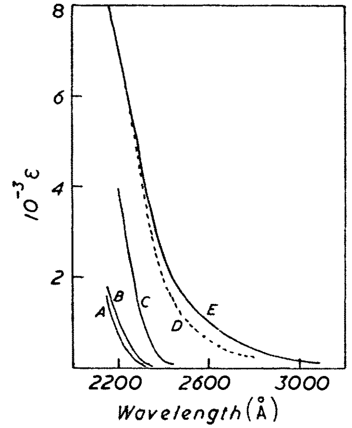


FIG. 3. *Absorption spectra of electron acceptors.*
A, Nitromethane vapour.
B, Nitromethane in *cyclo*hexane.
C, Tetranitromethane vapour.
D, Tetranitromethane in 2 : 2 : 4-trimethylpentane.
E, Tetranitromethane in *cyclo*hexane.

The results are shown in Fig. 3. Only a small (solvent) shift is observed for nitromethane, but with tetranitromethane the absorption at longer wavelengths is very much greater in *iso*octane and (especially) *cyclo*hexane than in the vapour phase. We have little doubt that this additional absorption is due to charge-transfer transitions, probably largely " contact charge-transfer spectra." These results for tetranitromethane are therefore consistent with the interpretation given for the iodine spectra. The ultraviolet absorption of tetranitromethane in aqueous solution has been measured by Kortüm;[21] his results resemble the vapour spectrum much more closely than the spectra obtained in *iso*octane or *cyclo*hexane solution. This is not unexpected in view of the very high ionisation potential of water (12·59 ± 0·01 v).

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INORGANIC CHEMICAL LABORATORY, OXFORD UNIVERSITY.
INORGANIC CHEMISTRY RESEARCH LABORATORIES,
IMPERIAL COLLEGE, LONDON, S.W.7.
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[18] Werner, *Ber.*, 1909, **42**, 4342; Heilbronner, *Helv. Chim. Acta*, 1953, **36**, 1121.
[19] Nicholson, *J.*, 1949, 1553.
[20] Haszeldine, *J.*, 1953, 2525.
[21] Kortüm, *Z. phys. Chem.*, 1939, **43**, *B*, 271.