or

$$\tau = \frac{1}{e^2}\left[E_i(2 - \ln \beta) - E_i(2)\right]$$

where $Ei(x)$ is the Integral Logarithm function.

For $\kappa = \infty$ the reaction again behaves as one of simple second order but here with the solution

$$\tau = \frac{1}{2}\left(\frac{1}{\beta} - 1\right) \quad \text{and } \alpha = \beta$$

EVANSTON, ILL.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, BROOKHAVEN NATIONAL LABORATORY]

Experiments on Compound Formation in Solutions at Low Temperatures. Iodine and Olefins[1]

BY SIMON FREED AND KENNETH M. SANCIER

Absorption spectra of solutions of iodine in olefins at temperatures from 77 to 230°K. show the presence of ultraviolet bands which match those of iodine in aromatic hydrocarbons previously reported. These bands had been proved characteristic of 1:1 molecular addition compounds between iodine and the hydrocarbons. Such addition compounds are formed by iodine with each of the following olefins examined either pure or dissolved in propane: propene, *cis*-butene-2, *trans*-butene-2, butadiene-1,3, 2-methylbutadiene-1,3. Cyclopropane also combines with iodine in the same way in agreement with the double-bond character often attributed to it. The addition compounds form reversibly. However, they require activation energy. At higher temperatures another type of reaction sets in decolorizing the iodine solutions, probably the halogenation across the double bond. Especially good evidence that the addition compound is an intermediate in the halogenation of the double bond is furnished by 2-methylbutadiene-1,3 and iodine. The heats of formation of the addition compound vary from 200 to 500 cal./mole. The nature of the bond in these compounds is discussed.

It is to be expected that compounds may form and persist at low temperatures which at higher temperatures would not be present in detectable quantities. The lower temperatures may therefore make possible the observation of weakly bonded substances and permit the study of reaction intermediates. We report here phenomena of this kind in reactions between olefins and iodine. In these systems we also have examples of the reduction to be generally expected in the number of competing reactions when the temperature is reduced.

Solutions of iodine in organic solvents have often been classified into those which give purple and those which give brown solutions, with the former exemplified for our purpose by iodine in hexane and the latter by its solutions in aromatic solvents such as benzene. Benesi and Hildebrand[2] have shown that in addition to the absorption band in the visible region, the brown solutions possess an extremely intense absorption peak in the ultraviolet and that this peak is to be ascribed to a 1:1 complex between iodine and the aromatic hydrocarbon. They regarded such a complex as a Lewis salt between the generalized acid and base, iodine and aromatic hydrocarbon, respectively.

Mulliken[3] viewed the intense absorption peak in the ultraviolet as a forbidden transition between the energy levels of the aromatic conjugated double-bond system made allowed by the presence of iodine.

Our experiments to discover whether olefins also enter into what we shall call addition compounds were carried out at low temperatures to increase their concentration and to avoid the well-known reactivity of halogens for the "double bond" at room temperature.

A double-beam Cary spectrophotometer was employed for measuring the spectra of the solutions in fused quartz tubes with light paths of 1 and of 8 mm. To eliminate the optical effect of the fused quartz, refrigerant, solvent, etc., the tubes were also measured with all but iodine present.

The iodine dried over phosphorus pentoxide was dropped into a tube previously filled with dried nitrogen. The tube was then evacuated while the iodine was kept at 193°K. By allowing the temperature to rise, the iodine was sublimed several times onto the surface of another part of the tube kept at 193°K. and any released gases were pumped off. The final sublimate was obtained as a film. The propane[4] was condensed upon the iodine at 193°K. Some time was required to form the purple solution. The corresponding condensation of propene led at once to a brown solution at the interface between the iodine and propene which quickly diffused into the body of the liquid.

The solutions in propane and also in propene were obtained easily as supercooled fluids at the temperature of liquid nitrogen. Solutions in mixtures of these hydrocarbons appear to be stable fluids even below the freezing point of nitrogen.[5]

All our operations were carried out in dim light to reduce any photochemical activity.

Propene and Propane.—At 230°K. the color of iodine in propane is purple with an absorption peak at 5200 Å. while its solution in propene is amber with a peak at 4800 Å. At 77°K. both solutions have about the same brown color and the absorption peak of the propene solution is at 4400 Å. We are uncertain of the position of the peak of the propane solution because at our concentration there was evidence of colloidal iodine at this temperature. The area "under" the visible band of iodine–propane changes little with temperature but that of iodine–propene increased two to three-fold when the temperature was reduced from 230 to 77°K. (Fig. 1). In the ultraviolet region, the iodine–propane solution at 230°K. exhibited no structure down to 2100 Å. but the iodine–propene solution showed a band at 2750 Å. about ten times as intense as its absorption in the visible. Both the intensity and wave length of the ultraviolet absorption match those of iodine in aromatic solvents as given by Benesi and Hildebrand and there seems no doubt that it arises from a corresponding iodine–propene addition compound.

At 230°K., our highest temperature, an irreversible reac-

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[1] Presented at the American Chemical Society Meeting, Chicago, Ill., September, 1950. Research carried out under the auspices of the U. S. Atomic Energy Commission.

[2] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[3] R. S. Mulliken, *ibid.*, **72**, 600 (1950). At the Chicago Meeting of the A.C.S., September, 1950, he presented a more general interpretation.

[4] All the hydrocarbons except cyclopropane were research grade (Phillips Petroleum Co.) further fractionated several times by distillation. Cyclopropane was obtained from Matheson Co., several times distilled from its solution of iodine.

[5] S. Freed and C. J. Hochanadel, *J. Chem. Phys.*, **17**, 664 (1949).

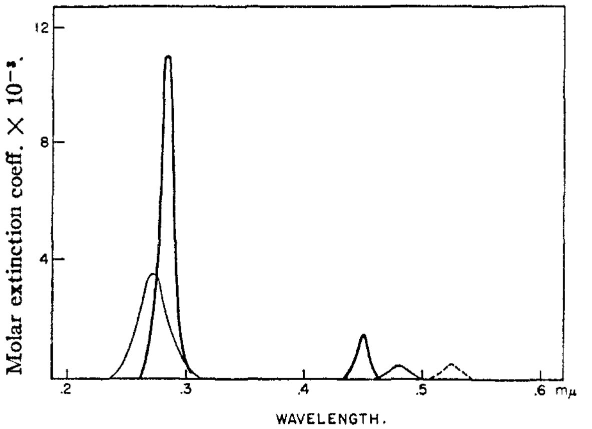


Fig. 1.—Absorption spectra of solutions of iodine in propane and with added propene at 230 and 77°K.

	77°K.	230°K
Propane		- - -
1:6, propene:propane	▬	—

tion set in slowly between the iodine and propene which decolorized the solution; that is, when the solution was cooled again the original band intensities were not restored; possibly diiodopropane had been formed. However, when the solvent propene was evaporated from the brown iodine solution at 193°K. it left a brown solid film behind and condensed as a colorless liquid which on recondensing on the film yielded a solution that had practically the original intensity in the absorption bands.

Similar experiments were carried out between iodine and the following hydrocarbons: *cis*-butene-2, *trans*-butene-2, butadiene-1,3, 2-methylbutadiene-1,3 and cyclopropane. In Table I are listed the wave lengths of the absorption peaks in the various liquids.

Table I

Absorption Peaks of Iodine[a] in Hydrocarbons

	Visible, Å.		Ultraviolet, Å.	
	230°K.	77°K.	230°K.	77°K.
Propane	5200	..	..	..
Propene	4800	4350	2700	2800
Cyclopropane (in propane)	5200	5000	2400	2400
	230°K.	150°K.	230°K.	150°K.
cis-Butene-2	4700	4550	2950	3000
trans-Butene-2	4750	4650	2970	2980
	230°K.	163°K.	230°K.	163°K.
Butadiene-1,3[b]	Reacts	4400	Reacts	2780
			193°K.	152°K.
Isoprene[c]	..	..	Reacts	3150

[a] All solutions are about 10^{-3} M iodine. [b] The relative molar concentrations of butadiene-1,3 in propane and propene in this solution are 1:13:55, respectively. [c] The relative molar concentrations of isoprene in propene and propane in this solution are 1:36:170, respectively.

Butene.—Each butene was condensed on a film of iodine at 193°K. dissolving the film at this temperature rather quickly. The solutions in a fused quartz cell were immersed in a coolant of pure propane which had been cooled by means of liquid nitrogen to 150°K. and the spectra of the solutions were taken.

The visible band of iodine in each isomer is essentially unaffected by temperature change. However, the ultraviolet band of the addition compound, iodine and *cis*-butene-2 is enhanced upon lowering the temperature to a considerably greater degree than that of iodine and *trans*-butene-2. Assuming that oscillator strengths are roughly equal, we conclude that the first addition compound is more stable than the second.

Butadiene.—At 193°K. butadiene dissolved iodine quickly and almost simultaneously reacted with it forming a colorless solution. The solubility of butadiene in propane at 77°K. was found to be slight; to increase its solubility some propene was added. The final solution was prepared as follows: A solution of iodine in 1:5 propene–propane and one of butadiene in the 1:5 hydrocarbon mixture were independently prepared. The two solutions were then combined at less than 150°K. to avoid the irreversible reaction. The temperature was raised for a minute or two to 195°K. and then quickly lowered to 77°K. and the spectrum was taken. The ultraviolet absorption band is at about the same wave length as the propene–iodine absorption but with about twice the intensity.

Isoprene (2-methylbutadiene-1,3) reacts as rapidly as butadiene-1,3 with a film of iodine at 193°K. producing a colorless solution. Such reactivity raised the question, how low a temperature would allow sufficient reactivity for the observation of the addition compound. For this purpose a rather high concentration of iodine was obtained by using a mixed solvent of propane and propene. After taking the spectrum of the iodine in this solvent at 77°K. for reference, one-third of the solvent was vaporized at 193°K., and to the gas phase isoprene was added. The gaseous mixture was totally condensed at 77°K. in the solution without appreciably raising the temperature of the residual solution and then mixed. The spectrum was then taken of the combined solution (5×10^{-3} M in iodine) in a solvent of the following proportions: iodine 1, isoprene 75, propene 2700 and propane 13,000. The spectrum proved to be the same as had been observed from the original solution not containing isoprene and it remained unchanged after the solution had been kept at 77°K. for two days. At a higher temperature, as we shall see, the reaction occurs and hence an energy of activation is necessary.

The temperature of the solution was then raised about 1 degree per minute, and spectra in the ultraviolet were constantly taken. The area under the propene–iodine band at

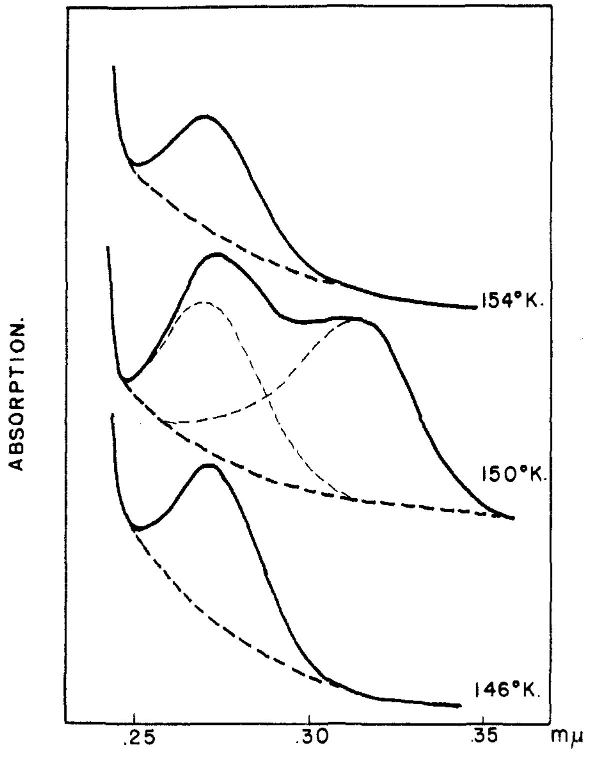


Fig. 2.—Absorption spectra of solution of iodine and 2-methylbutadiene-1,3 in propene and propane at three temperatures and the mole ratios in the same order are 1:75: 2700:13000. (Note: It was not possible to balance completely the double beam spectrophotometer for cell, solvent and coolant in this spectral region, and the heavy dashed-lines represent the absorption in the absence of iodine.)

2750 Å. decreases continuously when the temperature increases from 135°K. (the lowest temperature of this experiment) to 173°K. At 150°K. a new band appears at 3150 Å. and disappears at 154°K.; this is to be identified with the addition compound between iodine and isoprene. Figure 2 shows the change in the spectrum with temperature, and the dotted lines indicate the background and the components of the absorption at 150°K.

When this solution was brought to the reference temperature 77°K., the propene–iodine bands in the visible and ultraviolet were found to be half as intense as before the temperature had been raised. In the absence of isoprene, iodine and propene react only reversibly in this temperature range. From the decrease of the propene–iodine band with rise in temperature and the disappearance of the isoprene–iodine band at 150°K., it is concluded that the irreversible reaction between iodine and isoprene occurs at 150°K. and probably at lower temperatures. At 150°K. the rates of the competing reactions of the formation and of the disappearance of the addition compound were such as to make possible the observation of the 3150 Å. band.

Cyclopropane was studied because its properties have often been related to "double-bond character," strain, or hyperconjugation.

A solution of iodine in cyclopropane is purple, much like that of iodine in propane. In contrast to the latter, the solution in cyclopropane exhibits an ultraviolet absorption peak at 2400 Å., roughly five times as intense as the visible at (150°K.). The integrated intensity becomes considerably greater as the temperature is lowered as would be expected from an increase in concentration of the addition compound. With the view of working at lower temperatures than the freezing point of cyclopropane, we used as solvent for the iodine a 1:1 solution of cyclopropane and *n*-propane, in the following way: A solution of iodine in 2 cc. of *n*-propane was examined spectroscopically at about 130°K. One cc. of the *n*-propane was evaporated at 193°K. and in its place was condensed 1 cc. of cyclopropane. From Table II it is evident that the absorption at 2400 Å. represents the addition compound.

TABLE II

IODINE (10^{-3} *M*) IN 1:1 CYCLOPROPANE AND PROPANE

	Visible		Ultraviolet	
	230°K.	150°K.	230°K.	150°K.
Wave length, A.	5150	5000	2400	2400
Molar extinction coeff. (liter. moles^{-1} cm.$^{-1}$)	600	750	2900	5100

Heats of Formation.—The rough values of the heats of formation of the iodine–hydrocarbon addition compounds were determined from the variation with temperature of the integrated areas of the ultraviolet absorption bands, and the approximate values are +500 cal./mole for propene, cyclopropane and *cis*-butene-2, and +200 cal./mole for *trans*-butene-2. The values show little variation despite large differences in the intensities of the ultraviolet bands. At present we cannot distinguish between the influence of steric hindrance and density of charge at the double bond in their effects on the stability of the compounds with the geometric isomers of butene-2.

Discussion

One point is clear—aromatic character of the hydrocarbon is not necessary for formation of the addition compounds with iodine.

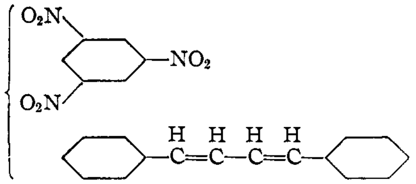
The designation of salt in the Lewis sense for the addition compound between iodine and an unsaturated hydrocarbon[6] seems to us to obscure important features of the bond.

From heats of solution of iodine in aromatic hydrocarbons[7] the heats of formation of the addition compounds have been estimated to be of the order of 1000 cal./mole. With olefins we find the heats of formation to be about 500 cal./mole. Such feeble binding can be accounted for in fair approximation, we believe, in terms of polarization and London dispersion energies. The electron density at the double bond in propene, for example, and somewhat similarly in the resonating electron systems of the aromatic hydrocarbons polarizes the iodine molecule leading to the formation of some of the dipole moment found by Fairweather. Even in the absence of this "static" classical polarization the London dispersion forces are not spherically symmetrical and hence no longer additive.[8] These forces may be associated with virtual electronics oscillators primarily in the bond structure of the molecule.

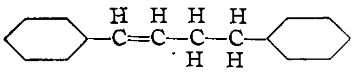
The energy of the London bonds depends on the magnitude of the oscillating electric moments, the mutual orientations and separations of the oscillators of the molecules and on the frequencies of the oscillations. We would at present stress this dynamic factor in binding which is not included in first approximation in the description of the state of the "acid" or "base" in terms of its resonance hybrids.

Somewhat similar situations seem to hold in the addition compounds between trinitrobenzene and aromatic conjugated double bond systems. These addition compounds resemble those of iodine with hydrocarbons in having characteristic spectra distinguishing them from their component molecules.[9]

The stability of the 1:1 compound in solution



has been found to be 2.88 kcal./mole while interruption of the chain of conjugate double bonds by hydrogenation



leads to a value of the heat of formation of 1.47 kcal. for the corresponding compound with trinitrobenzene. An increase in the length and hence strength of the oscillating electric moments augments the energy of the London bond. Also an increase in the stability of the bond arises from the decrease in frequency as the length of the chain increases.

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[6] (a) F. Fairweather, *J. Chem. Soc.*, 1051 (1948), and earlier work cited; (b) H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[7] K. Hartley and H. A. Skinner, *Trans. Faraday Soc.*, **46**, 621 (1950).

[8] F. London, *J. Phys. Chem.*, **46**, 305 (1942).

[9] G. Briegleb and J. Kambeitz, *Z. physik. Chem.*, **A32**, 305 (1936). These authors recognized the importance of the two factors we are discussing.