287. *Complex Formation between Polynitro-compounds and Aromatic Hydrocarbons and Bases. Part IX. The Influence of Solvents on the Temperature Coefficients of Colour Densities.*

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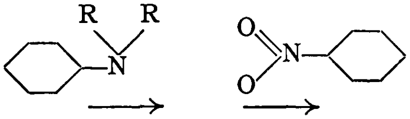
The effect of temperature change in various solvents has been studied for the following colour-producing interactions: tetranitromethane and naphthalene and α- and β-methylnaphthalenes; diphenylamine and *o*-chloronitrobenzene and chloro-2 : 4-dinitrobenzene. In certain polar solvents, positive temperature coefficients (colour increasing with temperature) have been observed for the tetranitromethane systems. These and other facts have been discussed in the light of the recent work of Gibson and Loeffler (*J. Amer. Chem. Soc.*, 1940, **62**, 1324).

The view has been developed by Briegleb (Ahrens Sammlung, Part 37, 1937) that the coloured products of the interaction of nitro-compounds with aromatic hydrocarbons and their derivatives, including the aromatic bases, are " polarisation aggregates " maintained by electrostatic forces between polar molecules (nitro-groups) and electric dipoles induced in the polarisable hydrocarbons. Briegleb is able to compute gram-molecular heats of interaction of the order of 2 kg.-cals. for assumed intermolecular distances of the order of 3 A. As the experimentally determined heats of interaction (see Baker and Bennett, *Ann. Reports*, 1931, **28**, 137, for bibliography) are of the order of 1—5 × 10^3 cals., and the law of force between the polarising and polarised molecules is according to the inverse sixth power, the inference is that the interacting molecules cannot possibly get as close together as is required for ordinary chemical-bond formation (1—2 × 10^{-8} cm.) between atoms in the separate molecules. This conclusion is supported by the crystallographic evidence, which is against bond distances between separate molecules in the solid complexes (Powell and Huse, *Nature*, 1939, **144**, 77).

The hypothesis of " polarisation aggregation " as the origin of the colour in the systems under consideration also implies that the activation energy for the interaction must be very small; this is borne out by the fact that the production of colour in nitro-compound–hydrocarbon mixtures is apparently instantaneous even at very low temperatures.* For instance, maximum colour is developed immediately when tetranitromethane is mixed with toluene at room temperature, and does not appear to be delayed when the admixture is brought about at —96° (m. p. of toluene).

The higher recorded values for the molecular heats of interaction (*e.g.*, — 3990 cals./g.-mol. for anthracene–picric acid in chloroform from the variation of colour with temperature; von Halban and Zimpelmann, *Z. physikal. Chem.*, 1925, **117**, 461) are of the same order as, but definitely lower than, the latent heats per g.-mol. of ordinary organic liquids. This implies that the forces operative between molecules to produce colour are no greater than those manifested between the molecules in any liquid and makes it probable that the colour-producing impacts differ in no way from ordinary impacts between liquid molecules, except that, in the former, more or less specific orientations will probably be necessary. This is the conclusion reached by a different route in an important paper by Gibson and Loeffler (*loc. cit.*), who assume "a drift of electronic charge from the NR_2 group to the oxygens of the NO_2 group with consequent displacements of negative charge in the N=O bond and in the polarisable aromatic nuclei," if present, in the sense indicated by the arrows:



This polarisation mechanism had already been suggested, as Gibson and Loeffler point out, by one of us (J., 1935, 580) as the primary activation in the formation of addition complexes derived from nitro-compounds, and is, in fact, the primary step in an oxidation–reduction reaction. Gibson and Loeffler regard this recession of negative charge in the nitro-compound as the probable cause of the observed colour changes. In this connection, some preliminary experiments in conjunction with Dr. F. M. Brewer † on mixtures of tetranitromethane and benzene in *n*-hexane indicate that the general absorption of the nitro-compound just outside the visible region is extended into the visible by the addition of the hydrocarbon, the absorption of which is apparently unaltered.

If the interactions responsible for the shift of absorption are " primary steps in possible reactions such as oxidation and reduction " (Gibson and Loeffler, *loc. cit.*), it follows that the significant groups and atoms in the separate molecules must approach more closely than in normal intermolecular impact. Messrs. H. M. Powell and G. Huse (private communication) find that in a number of solid nitro-compound–aromatic base complexes a shortening of the normal distances between the component molecules is required to obtain satisfactory interpretations of their *X*-ray analyses.

Briegleb's concept of coloured products of interaction in the kind of systems under discussion as " dipole aggregates " is difficult to reconcile with the observation that it is apparently only interactions between inducing and induced dipoles that are effective in producing colour. The polar nitro-groups in the molecules of different nitro-compounds must interact electrostatically; they do so without visible change in their absorption, even though the interaction is sufficient to allow the separation of homogeneous solid complexes (Hammick, Andrew, and Hampson, J., 1932, 171). Gibson and Loeffler's (*loc. cit.*) picture of the colour-producing mechanism as an incipient oxidation–reduction (acid–base) reaction makes a clear distinction possible between the two kinds of interaction and is in principle that of Moore, Shepherd, and Goodall (J., 1931, 1447), who regard " chemical " interaction alone as colour producing. Incipient chemical interaction of the kind postulated

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* Experiments have been reported (Hammick and Sixsmith, J., 1935, 580) in which indene and methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate apparently interact at measurable rates. In spite, however, of search over a wide field, no similar case has been discovered, and doubt must exist as to whether the data, which have been redetermined by Dr. Sixsmith, are not susceptible to some explanation other than that of slow interaction between nitro-compound and indene.

† It is hoped that these experiments may be repeated and extended in more opportune circumstances.

will occur whenever the appropriate atoms approach near enough under the influence of the thermal agitation even in liquid mixtures showing positive deviations from ideal behaviour; this is illustrated by the production of colour in solutions of methyl 4 : 6 : 4′ : 6′-tetranitrodiphenate in toluene, the components of which separate into two liquid layers on cooling (Hammick and Sixsmith, J., 1939, 972).

Gibson and Loeffler (*loc. cit.*) have observed that the absorption of light by certain binary mixtures of nitro-compounds and aromatic bases *increases* with rise in temperature at constant pressure. They direct attention to two opposing effects at work. In the first place, increase in free volume with rise in temperature " reduces the probability that two unlike molecules will be close together "; on the other hand, with increasing kinetic energy there will be greater intermolecular penetration and the molecules will " spend on the average a larger fraction of the time at very close quarters." We have examined the variation with temperature of the colours produced by the interaction of tetranitromethane with naphthalene and α- and β-methylnaphthalene; also of diphenylamine with mono- and di-nitrochlorobenzenes in a series of solvents. As will be seen (Tables I and II), the temperature coefficients of the colours of the systems containing diphenylamine are all negative, though the derived heats of interaction vary rather widely. The tetranitromethane systems, on the other hand, show negative or positive coefficients according to the solvent, the heats of interaction, ΔH, computed from the slopes varying from — 1040 cals. (naphthalene in hexane) to + 1640 cals. (α-methylnaphthalene in methyl alcohol).

EXPERIMENTAL.

The systems examined were (i) tetranitromethane and naphthalene or α- or β-methylnaphthalene; (ii) *o*-chloronitrobenzene and diphenylamine; and (iii) chloro-2 : 4-dinitrobenzene and diphenylamine, in the solvents shown in the tables. These particular reagents were selected because they are themselves colourless in the solvents selected but develop moderately intense orange-yellow colorations on admixture. Colour densities, D, were determined in a Hilger–Nutting spectrophotometer, the absorption tube being jacketed so that a stream of water at a known temperature could be circulated during the determinations. Each solution (5—10%) was maintained at temperatures at roughly 5° intervals between 15° and 60° for measurement; in all cases, the original colour density was regained on reverting to the original temperature. It was also found that the plots of log D against temperature were straight lines and parallel irrespective of (i) the relative amounts of nitro-compound and hydrocarbon or base and (ii) the wave-length at which the colour densities were determined. Lines in the blue or green region were found most suitable (λ between 4300 and 5200 A.).

The relation between the slope $\partial \log D/\partial T$ and $(\Delta H)_p$, the heat of interaction at constant pressure, is obtained as follows :—If A and B are colourless interactants that produce the coloured complex AB and set up the equilibrium defined by $K = [AB]/[A][B]$, then, as the amount of AB formed from original amounts of A and B is small, we have $K \propto [AB] \propto D$, on the assumption that the absorption of light is proportional to the concentration of coloured " impact complexes " ($D = \varepsilon cl$, the product of extinction coefficient, concentration and length of absorption tube). It follows therefore that $(\Delta H)_p = \boldsymbol{R}T^2(\partial \ln D/\partial T)_p$. Values for $(\Delta H)_p$ for $T = 20°$ are given in Table I. In Table II we give the photometric details of some of our experiments in order to exemplify their nature and scope.

TABLE I.

Values of $(\Delta H)_p$, *cals.*

	Tetranitromethane.			Diphenylamine.	
Solvent.	α-$C_{10}H_7Me$.	$C_{10}H_8$.	β-$C_{10}H_7Me$.	$C_6H_4Cl{\cdot}NO_2$.	$C_6H_3Cl(NO_2)_2$.
n-Hexane	—	−1040	—	−2240	−2520
CCl_4	− 960	− 980	−1040	−1100	−2080
$C_2H_4Cl_2$	—	− 320	—	− 920	−1000
$C_2H_2Cl_4$	—	− 200	—	− 740	− 880
COMePh	+1120	+ 760	+ 280	− 760	− 680
*cyclo*Hexanone	—	+ 720	+ 80	−1400	−1320
$COMe_2$	—	+ 560	+ 280	− 360	− 800
Pr^{a}OH	—	+ 800	—	− 320	−1480
EtOH	—	+1060	—	− 196	−1360
MeOH	+1480	+1120	+ 840	− 172	−1280

TABLE II.

Tetranitromethane–naphthalene. Solvent : *n*-hexane.

T	14·75°	25·5°	28°	32°	38°	45·75°	51·5°	55·5°	61·75°
log *D*	0·1751	0·1482	0·1459	0·1348	0·1225	0·1020	0·0795	0·0733	0·0641
T	18°	29·5°	35·5°	44°	48·5°	56°	59·75°		
log *D*	0·0802	0·0500	0·0252	0·0051	$\bar{1}$·9787	$\bar{1}$·9628	$\bar{1}$·9680		
T	16·5°	25·25°	28·6°	35°	41°	47·5°	53°	59·25°	
log *D*	$\bar{1}$·9186	$\bar{1}$·9025	$\bar{1}$·8820	$\bar{1}$·8663	$\bar{1}$·8525	$\bar{1}$·8439	$\bar{1}$·8091	$\bar{1}$·8048	

Mean slope = $-0·026$; $\Delta H = -1040$ cals.

Tetranitromethane–α-methylnaphthalene. Solvent : methyl alcohol.

T	15·0°	21·0°	26·0°	30·0°	35·0°	44·0°	47·5°	54·5°	58·5°
log *D*	0·1802	0·2076	0·2151	0·2305	0·2500	0·2767	0·2907	0·3090	0·3273
T	15·0°	21·0°	29·0°	36·0°	43·0°	45·0°	47·5°	54·5°	
log *D*	0·0422	0·0635	0·0983	0·1250	0·1526	0·1607	0·1688	0·1939	

Mean slope = $+0·0037$; $\Delta H = +1480$ cals.

Chlorodinitrobenzene–diphenylamine. Solvent : acetophenone.

T	16·0°	22·5°	28·0°	34·0°	37·5°	40·5°	44·0°	48·0°	50·0°	56·5°	61·5°
log *D*	0·0245	0·0199	0·0145	$\bar{1}$·9900	$\bar{1}$·9956	$\bar{1}$·9832	$\bar{1}$·9820	$\bar{1}$·9795	$\bar{1}$·9666	$\bar{1}$·9627	$\bar{1}$·9542
T	20·0°	22·5°	24·0°	28·0°	34·0°	38·0°	44·0°	47·5°	50·5°	57·5°	60·5°
log *D*	$\bar{1}$·9170	$\bar{1}$·9222	$\bar{1}$·9165	$\bar{1}$·9085	$\bar{1}$·8982	$\bar{1}$·8887	$\bar{1}$·8752	$\bar{1}$·8770	$\bar{1}$·8704	$\bar{1}$·8587	$\bar{1}$·8499

Mean slope = $-0·0017$; $\Delta H = -680$ cals.

Discussion of Results.

The first four solvents listed in Table I are " normal " liquids, having zero or very small electric dipole moments; in all of them it will be seen that the colour-producing interactions are exothermic, colour density *decreasing* with rise in temperature. It will also be noticed, on passing from left to right, that the heat evolved ($-\ \Delta H$) increases from the tetranitromethane systems to the chlorodinitrobenzene–diphenylamine systems in each solvent. Moreover, passing down the vertical columns, it appears that each of the interactions successively decreases in " exothermicity " in the same sequence of the first four solvents. It seems fair to conclude from this that (i) increase in free volume with temperature is more significant than the closer contacts that result from increased kinetic energy, and that (ii) the effect of free volume increase on colour decrease is much the same for each of the interactions.

The remaining six solvents are abnormal liquids. The polar carbonyl groups in the ketones must result in " dipole aggregation " and the alcohols are associated through hydrogen bonds. In all these solvents the tetranitromethane interactions are endothermic, colour *increasing* in intensity with temperature. The diphenylamine–nitro-compound interactions are all exothermic, though in both series the lowest observed values for $-\ \Delta H$ are in the polar solvents. Obviously, in such solvents the state of affairs is complex. Rise in temperature will break down large associated solvent complexes into smaller molecular units, which, packing closer, will result in diminution of free volume. It is possible that this is the explanation of the increase of colour with temperature in the tetranitromethane systems. The dipole moments of tetranitromethane and of the naphthalenes are zero or very small; dipole aggregation between solutes and polar solvents will therefore be negligible. This will not be so in the chloronitrobenzenes–diphenylamine systems in which the polar components will form dipole complexes with the polar solvent molecules. This effect will tend to diminish the number of colour-producing impacts between nitro-compound and base and will increase as rising temperature breaks down solvent dipole aggregates with low polarity into polar single molecules. It may be that herein lies the explanation of the fact that no endothermic interactions were observed in the polar chloronitrobenzene–diphenylamine systems.

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