Thermodynamic Parameters in the Conformational Equilibria of Acetyldiazomethane, 1-Acetyl-1-diazoethane, and Benzoyl(diazo)phenylmethane using Infrared Spectroscopy

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The integrated intensities of the two i.r. peaks resulting from the asymmetric N–N stretching vibration of acetyldiazomethane, 1-acetyl-1-diazoethane, and benzoyl(diazo)phenylmethane have been measured as a function of temperature in carbon tetrachloride. From the temperature dependence analysis of the relative areas, thermodynamic parameters for the *cis–trans*-conformational equilibria of these α-diazoketones have been obtained. Such parameters are discussed in terms of various contributions deriving from dipolar interaction forces and favourable steric arrangements which seems to indicate in the three cases a greater stability of the *cis*-conformer.

THE existence of conformational equilibria of type (1) in α-diazoketones, has been ascertained by using various physical techniques [1-7] and supported by MO calculations.[8,9] In a previous i.r. study of such equilibria,[10] diazoketones with a variety of R^1 and R^2 groups were investigated. Only for acetyldiazomethane, 1-acetyl-1-diazoethane, and benzoyl(diazo)phenylmethane was there observed doubling of the asymmetric N–N stretching band and variation with temperature in the relative peak intensities of the doublet components. This was interpreted to indicate that the three compounds contain two conformers, whilst all the other compounds investigated have only one, at room temperature and in CCl_4.

(1)

To complete this study, the present work reports values for the thermodynamic functions $\Delta G^{\ominus}$, $\Delta H^{\ominus}$, and $\Delta S^{\ominus}$ for conformational equilibria in the three title compounds. The functions were found by applying the method of integrated i.r. absorption to the two peaks of the asymmetric N–N absorption band. Only for acetyldiazomethane (diazoacetone) are such thermodynamic parameters known and these were determined from n.m.r. spectra below 0°.

EXPERIMENTAL

Acetyldiazomethane (I) was prepared by reaction of an excess of diazomethane with acetyl chloride in anhydrous ether [11] and was purified by distillation *in vacuo*. Its purity (>99%) was checked by g.l.c.

1-Acetyl-1-diazoethane (II) was prepared from 1-diazo-1-methylethane and acetyl chloride in anhydrous ether at $-40°$, in the presence of trimethylamine [12] and was purified by distillation *in vacuo*.

Benzoyl(diazo)phenylmethane (III) was prepared by oxidation of the corresponding monohydrazone with mercury(II) oxide.[13] Although the m.p. (64—65°; decomp.), the same for two different preparations, was lower than the literature value (79°; decomp.) the elemental analysis was as expected (Found: C, 75.45; H, 4.45; N, 12.35. Calc. for $C_4H_{10}N_2O$: C, 75.65; H, 4.55; N, 12.65%).

Samples were dissolved in CCl_4. Concentrations of the solutions were, at 20°, 0.012 59, 0.010 84, and 0.008 829M for compounds (I)—(III), respectively. Making due allowance for the changes in density of CCl_4 with temperature, solution concentrations were calculated using the equation reported in ref. 14 with the parameters d 1.632 55, α -1.9110, β -0.690, and γ 0. Measurements for compounds (I) and (II) were carried out between 30 and 60°. It was not possible to heat compound (III) above 30° because of decomposition, so the interval between -5 and $+25°$ was used.

To avoid alterations in concentration due both to prolonged standing and to transfer to the cells, the solutions were prepared and kept in containers of the type described by Nadeau and Jones.[15] Measurements were carried out on a PE model 521 spectrophotometer in NaCl cells having path lengths: sample cell 0.101 10, reference cell 0.100 96 cm. The cells were connected to thermostatted sleeves fed by water from an ultrathermostat giving a temperature accurate to ±0.1°. Before recording peak heights, the cells were exposed to i.r. irradiation for some time to ensure that thermal equilibrium between the thermostatted bath and the i.r. radiation was reached. Unfortunately, given the temperature interval studied, it was not possible to avoid spontaneous emission from the sample to the detector for samples (I) and (II) at higher temperatures. Temperatures were measured by a copper–constantan thermocouple kept in contact with a cell window.

Because of considerable overlapping of peaks (Figure) derived from the two conformers in all three cases, in order

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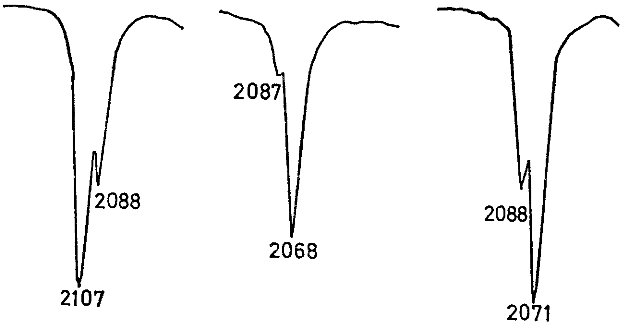
to measure their areas they had first to be separated using the method reported in ref. 16 after choosing the best baseline. Intensity data are reported in Tables 1 and 2.

Analysis of Data.—A typical treatment of the data for studies of this kind consists in the attribution of the two absorption bands to conformers C_1 and C_2 and then measuring the relative intensities of these bands as a function of temperature. The integrated intensity of each band is defined as $A = \alpha c_i d$, where α is the coefficient of integrated intensity, c_i the concentration of conformer i, and d the optical path of cell. Hence, the equilibrium constant, K for the reaction $C_1 \rightleftharpoons C_2$ is given by $K = c_2/c_1 = A_2\alpha_1/A_1\alpha_2$. Since integrated absorption coefficients usually cannot be measured, K is not calculated directly from this relation. Nevertheless, it seems reasonable to assume that the ratio of absorption coefficients is independent of temperature, at least for restricted temperature ranges, and in this case may easily be obtained from the Van't Hoff equations (1) and (2).



I.r. spectra of acetyldiazomethane (I), 1-acetyl-1-diazoethane (II), and benzoyl(diazo)phenylmethane (III) in the 2 150—2 000 cm^{-1} region

$$\ln K = -\Delta H^{\ominus}/RT + \text{constant} \tag{1}$$

$$\ln A_2/A_1 = -\Delta H^{\ominus}/RT + \text{constant}' \tag{2}$$

To calculate the functions $\Delta G^{\ominus}$ and $\Delta S^{\ominus}$, Hartmann *et al.*[17] proposed a method which also verifies the temperature invariance of the absorption coefficients. If c is the concentration of the solution, then $c = c_1 + c_2$, and this is true for all temperatures (below the decomposition temperature). Then equations (3) and (4) apply. Now,

$$A_1/\alpha_1 d + A_2/\alpha_2 d = c \tag{3}$$

$$A_1 = -\alpha_1 A_2/\alpha_2 + \alpha_1 dc \tag{4}$$

if the α values do not depend on temperature, a variation in the latter should produce only a variation in A_1 and A_2. Hence a plot of A_1 against A_2 at different temperatures will give a straight line of slope $-\alpha_1/\alpha_2$. The $\Delta G^{\ominus}$ and $\Delta S^{\ominus}$ values may readily be obtained using the ratio α_1/α_2 so obtained and equations (5) and (6).

$$\Delta G^{\ominus} = -RT\ln K = RT\ln A_2\alpha_1/A_1\alpha_2 \tag{5}$$

$$\Delta S^{\ominus} = (\Delta H^{\ominus} - \Delta G^{\ominus})/T \tag{6}$$

RESULTS

Figure 1 shows the absorption bands used to study the equilibrium for compounds (I)—(III). The study by Kaplan and Meloy[3] showed that, for diazoacetone, the *cis*-form is the most stable isomer at temperature below 0°. Analogous results have been obtained from dipole moment measurements at room temperature.[4] Hence, the intense band at 2 107 cm^{-1} in CCl_4, which decreases with increase in temperature, is assigned to the *cis*-conformer and that at 2 088 cm^{-1}, which increases with temperature, is assigned to the *trans*-conformer.

TABLE 1

Band areas and derived thermodynamic properties for the conformational equilibria of acetyldiazomethane and 1-acetyl-1-diazoethane

	CH_3COCHN_2			$CH_3COC(CH_3)N_2$		
T/°C	A_1 (2 107 cm^{-1})	A_2 (2 088 cm^{-1})	K [a] = *trans*/*cis*	A_1 (2 087 cm^{-1})	A_2 (2 068 cm^{-1})	K [b] = *trans*/*cis*
30	186.7	100.5	0.262	10.5	98.0	0.098 3
35	186.3	102.3	0.267	11.3	97.5	0.106 3
40	186.0	104.7	0.274	12.0	97.0	0.113 5
45	184.3	106.6	0.282	13.0	96.0	0.124 2
50	183.1	108.6	0.289	14.0	95.0	0.135 2
55	182.4	109.5	0.292	14.5	94.5	0.140 8
60	182.0	111.2	0.298	15.0	94.0	0.146 4
			Error [c]		Error [c]	
α_1/α_2		0.487		1.090		
$\Delta G^{\ominus}$/kJ mol^{-1}		3.36	0.06	5.54	0.06	
$\Delta H^{\ominus}$/kJ mol^{-1}		3.67	0.84	11.63	1.05	
$\Delta S^{\ominus}$/J K^{-1} mol^{-1}		0.96	2.51	19.12	2.68	

[a] Error in K ±0.006 calculated on basis of 1% error in band areas [b] Error in K ±0.003 calculated on basis of 1% error in band areas. [c] From the equation given in ref. 24.

For 1-acetyl-1-diazoethane (II) and benzoyl(diazo)phenylmethane (III) assignment of the two i.r. peaks to the possible conformers is not easy. In fact, the presence in these compounds of effects of a different nature than that of diazo–carbonyl conjugation, caused by steric interaction between methyl and phenyl groups, allows the possibility that non-planar conformers exist. For biacetyl, a molecule structurally very similar to compound (II), there is disagreement in the literature on the conformers present.[18,19] For 1-acetyl-1-diazoethane (II) recent CNDO/2 calculations[9] have, nevertheless, shown that *cis*- and *trans*-forms probably exist in equilibrium, stabilised by diazo–carbonyl

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resonance, the *cis*-form being predominant. On the basis of this calculation and also taking into account the thermal behaviour of the band areas, we have assigned the intense band at 2 068 cm^{-1} to the *cis*-conformer and the weak absorption at 2 087 cm^{-1} to the *trans*.

TABLE 2

Band areas and derived $\Delta H^{\ominus}$ value for the equilibrium of benzoyl(diazo)phenylmethane

T/°C	A_1(2 088 cm^{-1})	A_2 (2 071 cm^{-1})	A_1/A_1
25	51.3	117.3	2.29
20	55.6	118.0	2.12
15	57.0	113.3	1.99
10	62.5	116.5	1.86
5	71.5	126.6	1.77
0	81.0	135.0	1.67
−5	88.5	135.5	1.53

$\Delta H^{\ominus}$ = 8.7 kJ mol^{-1} (estimated error ±2 kJ mol^{-1}).

There is no literature data for benzoyl(diazo)phenylmethane which might help in assigning the two peaks of the asymmetric N–N stretching vibration. However, by analogy with the assignments for (I) and (II) we assign the more intense band (2 071 cm^{-1} in CCl_4) to the *cis*-conformer (or a structurally very similar conformer).

It is evident from Tables 1 and 2 that, whilst variation in band areas with temperature is more or less regular for molecules (I) and (II), for benzoyl(diazo)phenylmethane both areas change in the same sense indicating onset of decomposition at higher temperature. Under these conditions, it is not possible to calculate K since the α_1/α_2 ratio cannot be obtained from the A_1 against A_2 plot. Thus, only an approximate value of $\Delta H^{\ominus}$ has been evaluated for this molecule. For acetyldiazomethane a plot of the 2 107 cm^{-1} band area against the area of the 2 088 cm^{-1} band, gives a straight line with a good correlation (r −0.974) with the regression equation $A_1 = 236.111 - 0.487A_2$. For 1-acetyl-1-diazoethane a similar plot also gives excellent linearity (r −0.997; $A_1 = 117.507 - 1.090A_2$).

From the slopes of these lines the equilibrium constants have been calculated and are shown in Table 1. The $\Delta H^{\ominus}$ functions for the three molecules were calculated from the plots of $\ln A_1/A_2$ against $1/T$, for which the regression equations are given in Table 3. The $\Delta S^{\ominus}$ values for molecules (I) and (II), found using the $\Delta H^{\ominus}$ functions and the $\Delta G^{\ominus}$ values obtained from the equilibrium constants are in Table 1.

TABLE 3

Regression equations and correlation coefficients of plots $\ln A$(*cis*)/A(*trans*) against $1/T$ for molecules (I)—(III)

Compound	Intercept	Slope	Correlation coefficient
(I)	−0.837	0.441×10^3	0.996
(II)	−2 379	1.397×10^3	0.994
(III)	4.269	-1.030×10^3	−0.998

DISCUSSION

The results will first be compared with the measurements carried out between −40 and 0° on diazoacetone by Kaplan and Meloy;[3] then the thermodynamic functions for the conformational equilibria of the three molecules will be compared with one another.

$\ln K$ Values have been plotted against $1/T$ (r —0.996; $\ln K = 0.135—447.099/T$). The K value at −40°, obtained by extrapolating this plot (0.168), is consistent with that of Kaplan and Meloy (0.180),[3] especially taking into account their use of a different technique and solvent. Obviously, K, expressed as *trans*/*cis*, increases with temperature since heating produces a relaxation of the electrostatic forces of the diazo–carbonyl dipolar interaction which stabilises the *cis*-conformer of diazoacetone (and of the other diazoketones investigated) at lower temperatures. Obviously, this is not the only factor in play; it is necessary to invoke other effects in order to explain the differences in $\Delta H^{\ominus}$ values for the three molecules.

For diazoacetone it is not possible to invoke steric hindrance which might alter the planarity of the molecule. Consequently, the *cis*-conformer, although stabilised by dipolar interactions, is at an energy not very different from that of the *trans*-conformer, as demonstrated by the low $\Delta H^{\ominus}$ value and by the fact that the two conformers have practically the same entropy between 30 and 60°.

For 1-acetyl-1-diazoethane the situation is somewhat more complex, and the high $\Delta H^{\ominus}$ value requires explanation. At first sight, the higher stability of the *cis*-form appears surprising given the steric hindrance present, since it has been demonstrated[20] that the electron clouds of two *cis*-methyl groups should interpenetrate by *ca.* 1.2 Å. Probably, the validity of such an approach is questionable since it may be used only if the methyl group is considered to be a rigid sphere. In fact, it has recently been demonstrated by Sorriso *et al.*[9] that the two methyl groups of 1-acetyl-1-diazoethane preferentially arrange themselves, in the *cis*-conformation, in a star position so as to minimise repulsion. This gives rise to a *cis*-configuration which is strongly stabilised with respect to the *trans*, greater than if, even in the same configuration, the two methyl groups were in an eclipsed position. In addition, the calculated stabilisation energy,[9] 10.4 kJ mol^{-1} is comparable, within experimental error, with the $\Delta H^{\ominus}$ value found here. This would confirm the suggestion that there is additional stabilisation of the *cis*-form with respect to the *trans* due, in this molecule, to the star configuration of the two *cis*-methyl groups.

For this molecule the entropy variation is surprisingly high, especially if compared with the corresponding value for diazoacetone. This is possibly due to effects acting in the opposite sense. In fact, because of interpenetration by the two methyl groups, the *cis*-form of 1-acetyl-1-diazoethane is characterised by a more ordered structure, and hence lower entropy content, compared to the *cis*-form of diazoacetone. In contrast, the *trans*-form of 1-acetyl-1-diazoethane would have a higher entropy than the *trans*-conformer of diazoacetone since the presence of a methyl group in place of the methyne hydrogen introduces greater orientational disorder.

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Finally, for benzoyl(diazo)phenylmethane, the value for $\Delta H^{\ominus}$ of 8.7 kJ mol^{-1} is more easily understandable, even though a strictly quantitative explanation is not possible. Such a high value compared with that for diazoacetone suggests that factors other than dipole interaction of the diazo–carbonyl system contribute in some way to stabilise the *cis*-form. It is clear that a stable *cis*-form may be formed only if the two phenyl groups are arranged in a face-to-face position and are not coplanar. This is possible only if the rings are tilted by 90° about the C–Ar bond. Under these conditions the interatomic distances for the two phenyl rings should be comparable to those for dibenzil in the synperiplanar configuration.[21] For the last mentioned molecule it has been suggested[22,23] that the C(1) and C(4) orbitals (see Figure 2 of ref. 21), if correctly oriented, should give rise to an effective overlap calculated from MO calculations to give a 'bonding' energy of 3.72 kJ mol^{-1} for the interaction between the two benzene nuclei. If we now add this value for the interaction between the two phenyl rings to the $\Delta H^{\ominus}$ value obtained for diazoacetone, which we believe is due to contributions from electrostatic interactions alone, we obtain a stabilisation energy for the *cis*-form that is very similar to that for $\Delta H^{\ominus}$ obtained experimentally for the *cis* ⟶ *trans* conversion of benzoyl(diazo)phenylmethane.

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