Reactions at High Pressure. Part 15.† Rates, Activation Parameters, and a Volume Profile for Retro-Diels–Alder Reactions in the Pyrrole Series

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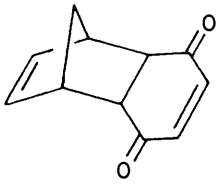
Thermal decomposition of *N*-acylpyrrole adducts of *N*-phenylmaleimide by a $[_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s]$ route occurs at temperatures below 70 °C. Rates and activation parameters for the thermolyses of *endo*- and *exo*-10-benzoyl-4-phenyl-4,10-diazatricyclo$[5.2.1.0^{2,6}]$dec-8-ene-3,5-dione (**6**) and (**7**), *exo*-10-acetyl-4-phenyl-4,10-diazatricyclo$[5.2.1.0^{2,6}]$dec-8-ene-3,5-dione (**8**), and *endo*-4-phenyl-4-aza-10-oxatricyclo[5.2.1.0]dec-8-ene-3,5-dione (**9**) have been measured at various temperatures and pressures and in various solvents. It is confirmed that the volume of activation for thermolysis of (**6**) is negative, consistent with a transition state more compact than either reagents or products and not accountable for in terms of dipolar character.

The Diels–Alder reaction has been extensively investigated by high-pressure kinetics in solution; volumes of activation typically lie in the range -30 to -40 cm^3 mol^{-1}.[1] In several cases, volumes of reaction have also been determined; these may be less negative than $\Delta V^{\ddagger}$ by 1—5 cm^3 mol^{-1}, though this is not universal. An observation of this kind implies that the transition state is more compact than the product; possible reasons for this could include dipolar character of the transition state or additional transannular bonding, *i.e.* 'secondary overlap' between π-orbitals of the dienophile and C(2),C(3) of the diene, inferred by Woodward and Katz[2] as a directing influence towards *endo*-addition. Dipolar character of the transition state is usually discounted on the grounds of insensitivity of rates of reaction to solvent polarity.

Whereas the volume of activation is obtained from kinetic measurements, the volume of reaction is deduced from solution densities. These constitute two large quantities, obtained by unrelated methods, so that the small difference between them is subject to considerable uncertainty. A less equivocal demonstration of the volume minimum at the transition state would be the observation of a negative volume of activation for the retro-reaction.

The reverse or retro-Diels–Alder reaction of necessity traverses the same reaction pathway as the forward reaction, and is equally orbital-symmetry permitted, $[_{\pi}2_s + {}_{\sigma}2_s + {}_{\sigma}2_s]$. It is of importance as a synthetic route to dienes,[3] but in most cases takes place readily only at elevated temperatures (200—500 °C). Examples of adducts which undergo thermolysis at temperatures below 100 °C are few and include structures (**1**)—(**5**).[4—7] Consequently there is relatively little kinetic information available on liquid-phase reactions of this type. It is notable that entropies of activation tend to be very small or slightly negative, whereas the enthalpy of reaction is large and positive. Exothermicity implies, by the Hammond postulate, an early transition state, reactant-like with respect to nuclear positions, whereas a small or negative entropy of activation confirms that bond fission has not proceeded to any great extent and may possibly show a further restriction of internal motion. Only one measurement of a volume of activation for a retro-Diels–Alder reaction has been reported: Jenner *et al.* studied pressure effects on the decomposition of a mixture of *exo*- and *endo*- (**5**) and found $\Delta V^{\ddagger}$ *ca.* -2 cm^3 mol^{-1}.[5]

We have recently prepared Diels–Alder adducts of acylpyrroles using high-pressure conditions,[8] and have found many of the adducts, especially those with maleic anhydride or *N*-phenylmaleimide, to be thermally labile and therefore suitable subjects on which to make measurements of activation parameters and solvent effects for retro-Diels–Alder reactions. These measurements are reported here.



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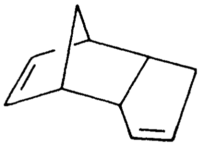

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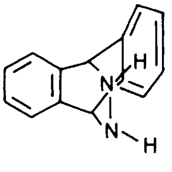

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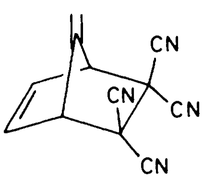

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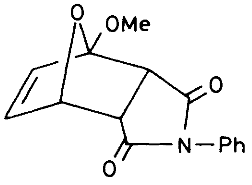

(5)

Experimental

Diels–Alder adducts were prepared from reactions between the appropriate pyrrole or furan and *N*-phenylmaleimide at pressures around 1.4 GPa as previously described.[8] Rates of decomposition to the precursors were measured by observation of the increase of absorbance at 318 nm due to formation of *N*-phenylmaleimide. Rate measurements at high pressures (to 1 kbar) were carried out in the apparatus previously described,[9] temperatures being controlled to within ±0.1 °C. Rate constants

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† Part 14, N. S. Isaacs and T. Najem, *J. Chem. Soc., Chem. Commun.*, 1984, 1362.

were calculated by the Guggenheim method,[10] to a least-squares fit for which correlation coefficients were usually better than 0.99. Activation parameters were calculated from the Arrhenius equation and entropies of activation from equation (1), in which $\langle T \rangle$ was taken as 300 K. Results are summarised in Tables 1—3.

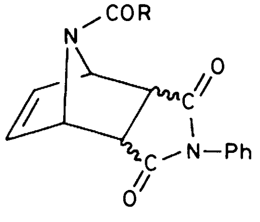
$$\log(A/\mathrm{s}^{-1}) = \log(ek\langle T\rangle)/h + (\Delta S^{\ddagger}/\mathrm{J\,K^{-1}\,mol^{-1}})/(R/\mathrm{J\,K^{-1}\,mol^{-1}} \times 2.303) = 13.23 + \Delta S^{\ddagger}/19.147 \quad (1)$$

Discussion

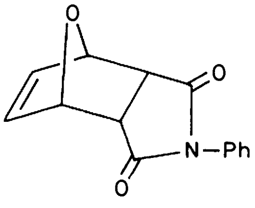
The decompositions of the adducts (**6**)—(**9**) occurred with satisfactory first-order kinetic relationships to at least 80% reaction. From the rates at 30 °C (Table 2) it appears that the reactions are rather indifferent to the nature of the solvent, the extremes for (**6**) differing by no more than a factor of 2.5, though this becomes 50 for adduct (**7**). There is no discernible correlation of rate with polarity of the solvent as measured by E_T[11] nor with π^*,[12] though a dual-parameter correlation using

Table 1. Rates of unimolecular decomposition of Diels–Alder adducts (**6**)—(**9**) temperature and solvent effects

Solvent	T/°C	$10^5\ k/\mathrm{s}^{-1}$	10^6 (Std. devn.)	Corr. coefft.
Adduct (**6**)				
$CHCl_3$	30.7	7.9	0.870	0.9994
	37.1	18.3	1.94	0.9990
	46.4	58.3	4.82	0.9997
	51.9	120	6.38	0.9999
CH_2Cl_2	22.1	1.06	0.277	0.9950
	27.8	4.32	0.474	0.9994
	32.4	7.42	0.414	0.9998
AcOEt	35.0	8.08	2.05	0.9949
	40.0	16.6	1.78	0.9993
	46.1	35.0	0.99	0.9971
	54.8	78.3	7.10	0.9995
MeCN	35.1	4.93	0.47	0.9994
	41.6	14.0	1.65	0.9994
	52.2	41.7	2.48	0.9999
	69.9	287	79.7	0.9973
Me_2SO	44.5	20.0	2.94	0.9992
	56.5	102	28.7	0.9969
	72.8	492	125	0.9977
Dioxane	31.0	5.43	1.04	0.9991
	41.3	21.6	2.22	0.9996
	57.5	137	28.0	0.9982
	67.95	432	21.1	0.9999
THF	23.8	2.23	0.202	0.9986
	30.4	5.30	0.648	0.9990
	38.9	18.3	2.78	0.9988
	52.9	86.6	14.6	0.9986
	67.0	500	77.7	0.9992
Adduct (**7**)				
Me_2SO	71.7	5.33	2.54	0.9922
	97.3	31.7	26.9	0.9809
	110.0	61.7	18.7	0.9964
	138.0	315	79.5	0.9978
Dioxane	71.0	1.37	0.758	0.9820
	75.0	2.88	1.35	0.9903
	78.0	4.75	0.680	0.9929
	84.0	13.0	38.1	0.9917
	95.0	26.6		0.9198
Adduct (**8**)				
Me_2SO	55.8	3.0	0.867	0.9955
	65.4	8.6	0.585	0.9998
	68.2	23.3	19.7	0.9831
	93.5	102	37.1	0.9928
	110.0	330	95.6	0.9975
Dioxane	71.0	23.3	5.27	0.9986
	76.5	33.3	17.2	0.9916
	83.0	96.6	25.2	0.9976
	85.5	110	33.2	0.9973
Adduct (**9**)				
$CHCl_3$	43.0	2.72	0.640	0.9967
	52.9	6.98	1.67	0.9980
	55.0	11.0	2.02	0.9987
	65.0	21.7	34.3	0.9280



(**6**) *endo*, R = Ph
(**7**) *exo*, R = Ph
(**8**) *exo*, R = Me



(**9**)

Table 2. Activation parameters for the decomposition of the Diels–Alder adducts (**6**)—(**9**)

Solvent	Rate k_{30}/s^{-1}	Arrhenius gradient	$\log A$/s^{-1}	E_a[a]/$\mathrm{kJ\,mol^{-1}}$	$\Delta S^{\ddagger}$[a]/$\mathrm{J\,K^{-1}\,mol^{-1}}$
Adduct (**6**)					
$CHCl_3$	7.18	−5.47	13.9	104 ± (2)	12.8 ± (4)
CH_2Cl_2	4.66	−6.22	16.2	81 ± (4)	57 ± (5)
AcOEt	4.69	−5.03	12.2	96 ± (6)	−18 ± (18)
MeCN	2.84	−5.24	12.7	100 ± (4)	−10 ± (12)
Me_2SO	3.38	−5.37	13.2	102 ± (7)	0 ± (22)
Dioxane	4.89	−5.30	13.2	101 ± (1)	−1 ± (4)
THF	5.24	−5.45	13.7	104 ± (2)	9 ± (6)
Adduct (**7**)					
Me_2SO	0.164	−3.76	6.6	72 ± (2)	−126 ± (4)
Dioxane	0.003 30	−6.89	15.3	132 ± (15)	39 ± (4)
Adduct (**8**)					
Me_2SO	0.274	−4.53	9.3	86 ± (9)	−71 ± (26)
Dioxane	0.0790	−6.17	14.3	118 ± (13)	20 ± (9)
Adduct (**9**)					
$CHCl_3$	0.706	−4.43	9.5	84 ± (8)	−73 ± (25)

[a] Error limits quoted correspond to one standard deviation (68% confidence) in a least-squares fit.

Table 3. Effect of pressure on the decomposition of (**6**) in $CHCl_3$ at 38 °C

p/bar	1	300	500	1 000	1 250
$10^4k/\mathrm{s}^{-1}$	1.20	1.32	1.50	1.67	1.83

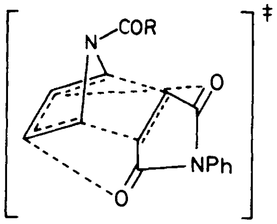
$\Delta V^{\ddagger} = -8.3 \pm 0.7\ \mathrm{cm^3\,mol^{-1}}$

Partial molar volumes, $CHCl_3$ (25 °C)	$\bar{V}/\mathrm{cm^3\,mol^{-1}}$
N-Phenylmaleimide	140.4 ± 0.2
N-Benzoylpyrrole	143.4
Adduct (**6**)	261.4
Volume of reaction, V,	+22.4

π^* and the Hildebrand solubilty parameters δ[13] produced the regression of equation (2), significant at the 5% level ($F = 11.4$).

$$\ln k = (3.42 \pm 0.42) + (1.40 \pm 0.57)\pi^* - (0.28 \pm 0.06)\delta \quad (2)$$

This type of correlation has been observed previously[14] for Diels–Alder reactions in the forward direction when the coefficient of δ is positive, but any mechanistic conclusions from so small a data set would be unwarranted. However, the activation parameters give evidence of considerable differences in the nature of solvation in the transition states with change in solvent. Entropies of activation in particular, which might be expected to be positive, vary widely and, even allowing for quite large error limits, in some cases are negative. Particularly interesting in the behaviour of the *endo*/*exo* pair of isomers, (**6**) and (**7**). Rates of decomposition of the *endo*-compound are considerably greater than those of the *exo*, and entropies of activation of the former are near zero both in Me_2SO and in dioxane, resembling in this respect other retro-Diels–Alder reactions in the gas phase or in benzene.[3] The *exo*-isomer shows a 50-fold acceleration in Me_2SO as compared with dioxane on account of a more favourable activation energy, but offset by a very negative entropy. It appears that decomposition of (**7**) is facilitated by strong, specific solvation of the transition state by Me_2SO though not by dioxane, whereas reaction of (**6**) is able to proceed assisted by interactions across the bicyclic system which make the transition state much less prone to solvation effects. Distinct mechanistic pathways appear to be used by the two isomers. The pressure dependence on the rate of (**7**) establishes that the partial molar volume of the transition state is less than that of the reagent, $\Delta V^‡ = -8.3 \pm 0.7\ cm^3\ mol^{-1}$. This measurement was made in chloroform for which $\Delta S^‡ = +12.8 \pm 4\ J\ K^{-1}\ mol^{-1}$, suggesting that no especially large solvation term is present. This observation is therefore attributable to an intrinsic effect, activation accompanied by transannular attractive forces between the carbonyl groups of the *N*-phenylmaleimide moiety and positions 3 and 4 of the pyrrole ring [see (**10**)].



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