Reactions of Aryl Isothiocyanates with Dicyclohexylcarbodi-imide. Search for the Mechanism of Cycloaddition and Cycloreversion

By **Alessandro Dondoni,*** Istituto di Chimica Organica, Università, Viale Risorgimento 4, 40136 Bologna, Italy
Arturo Battaglia, Laboratorio dei Composti del Carbonio contenenti Eteroatomi, C.N.R., 40064 Ozzano E., Italy

The [2 + 2] thermal cycloadditions of dicyclohexylcarbodi-imide (DCC) with *para*-substituted phenyl isothiocyanates (NO_2, Cl, H, OMe, or NMe_2) give 1 : 1 adducts, all showing spectral characteristics of 1,3-thiazetidine derivatives. The reactions are reversible. The kinetics of the forward and reverse reactions of a selected example (p-$O_2NC_6H_4N{=}C{=}S$ with DCC) were measured at different temperatures in four solvents (cyclohexane, carbon tetrachloride, butan-2-one, and acetonitrile); the equilibrium constants were determined under the same conditions. The absence of a substantial solvent effect on rate, as well as the failure of trapping experiments point to concerted cycloaddition and cycloreversion reactions with differing degrees of bond formation (or breaking) at the reaction termini in the transition state. Alternative mechanisms *via* open-chain intermediates are not definitively ruled out.

AMONG the variety of cycloaddition reactions, the [2 + 2] cycloadditions of cumulenes [1] are of current interest since they provide a general route to four-membered ring compounds and constitute a testing ground for theoretical arguments of chemical reactivity. The stereochemistry and the orientation of the reactants, as well as the concerted or stepwise nature of the mechanism of these reactions, are the subject of stimulating investigations.[2] The important prediction based on orbital symmetry selection rules,[3] that the [2 + 2] cycloadditions of a cumulated system such as a keten or an allene can occur by a supra-antara pericyclic process has been experimentally ascertained in several cases, and extended to other cumulenes. Selected examples of one-step [2 + 2] cycloadditions are the dimerization of ketens [4a] and their reactions with azo-compounds,[4b] alkenes,[4c] and enol ethers,[4d] the dimerization of allenes [4e] and some of their reactions with activated olefins,[4f] and the cycloadditions of ketenimines with azobenzenes.[4g] However, equally numerous are the cases where a two-step mechanism *via* open-chain intermediates, dipolar or diradical, has been advanced [5a]; these include the cycloadditions of sulphonyl isocyanates [5b] and diphenylketen [5c] with carbodi-imides, the cycloadditions of electron-deficient and electron-rich allenes with multiple-bond systems,[5d] and the cycloadditions of arylketens with 1,1-dimethylallene.[5e] Evidence that additions of ketens to olefins may proceed stepwise rather than concertedly has also been presented.[5f] Finally, examples of the competitive occurrence of both mechanisms are also known.[6] It thus appears that [2 + 2] cycloadditions of cumulenes can follow both reaction pathways, structural features of the reactants probably dictating which is preferred.

Mechanistic studies mainly concern the cycloadditions of ketens and allenes whilst for other cumulenes the investigations are more scanty. We now report some studies on the thermal isothiocyanate–carbodi-imide cycloaddition and cycloreversion which substantiate the assumption of essentially concerted processes.

RESULTS AND DISCUSSION

The cycloadditions of isothiocyanates (1) activated by electron-withdrawing groups (p-nitrophenyl, alkyl- and aryl-sulphonyl) with carbodi-imides (2) give [7] four-membered ring 1 : 1 adducts with the 1,3-thiazetidine structure (3) instead of the 1,3-diazetidine (4) previously assumed.[8] Similarly, other aryl isothiocyanates (1b—e) including those with electron-releasing substituents, such as OMe and NMe_2, were found to react with dicyclohexylcarbodi-imide (DCC) to form 1 : 1 adducts in variable yields (30—50%). At present, proof of structure of the new 1,3-thiazetidine derivatives † (3b—e) rests on their spectral similarities with other products previously described [7] (Table 1). Dipole moment data provide further support for the assignments.[9] Hence, at

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† These adducts may be composed of stereoisomers, but in the present context are treated as homogeneous species.

[1] H. Ulrich, 'Cycloaddition Reactions of Heterocumulenes,' Academic Press, New York, 1967; L. L. Muller and J. Hamer, '1,2-Cycloaddition Reactions,' Interscience, New York, 1967.

[2] P. D. Bartlett, *Quart. Rev.*, 1970, **24**, 473.

[3] R. B. Woodward and R. Hoffmann, 'The Conservation of Orbital Symmetry,' Academic Press, New York, 1970, p. 163.

[4] (*a*) R. Huisgen and P. Otto, *J. Amer. Chem. Soc.*, 1968, **90**, 5342; E. V. Dehmlow, *Tetrahedron Letters*, 1973, 2573; (*b*) R. C. Kerber and T. J. Ryan, *ibid.*, 1970, 703; (*c*) R. Montaigne and L. Ghosez, *Angew. Chem. Internat. Edn.*, 1968, **7**, 221, 643; R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, 1969, **102**, 3391, 3444, 3475; N. S. Isaacs and P. Stanbury, *J.C.S. Perkin II*, 1973, 166 and references therein; J. E. Baldwin and J. Kapecki, *J. Amer. Chem. Soc.*, 1969, **91**, 3106; (*d*) J. C. Martin, V. W. Goodlett, and R. D. Burpitt, *J. Org. Chem.*, 1965, **30**, 4309; W. T. Brady and R. O'Neal, *ibid.*, 1967, **32**, 612; R. Huisgen, L. A. Feiler, and P. Otto, *Chem. Ber.*, 1969, **102**, 3405, 3444, 3460; (*e*) C. W. N. Cumper, Z. T. Fomum, P. M. Greaves, and S. R. Landor, *J.C.S. Perkin II*, 1973, 885 and references therein; (*f*) E. F. Kiefer and M. Y. Okamura, *J. Amer. Chem. Soc.*, 1968, **90**, 4187; (*g*) M. W. Barker and R. H. Jones, *J. Heterocyclic Chem.*, 1972, **9**, 555; R. C. Kerber, T. J. Ryan, and S. D. Hsu, *J. Org. Chem.*, 1974, **39**, 1215.

[5] For leading references see (*a*) R. Gompper, *Angew. Chem. Internat. Edn.*, 1969, **8**, 312; (*b*) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Amer. Chem. Soc.*, 1968, **90**, 528; (*c*) W. T. Brady and E. D. Dorsey, *J. Org. Chem.*, 1970, **35**, 2732; (*d*) R. Gompper and D. Lach, *Angew. Chem. Internat. Edn.*, 1971, **10**, 70; 1973, **12**, 567; (*e*) P. R. Brook, J. M. Harrison, and K. Hunt, *J.C.S. Chem. Comm.*, 1973, 733; (*f*) H. U. Wagner and R. Gompper, *Tetrahedron Letters*, 1970, 2819.

[6] R. Huisgen and P. Otto, *J. Amer. Chem. Soc.*, 1969, **91**, 5922; E. Schaumann, S. Sieveking, and W. Walter, *Tetrahedron Letters*, 1974, 209.

[7] (*a*) I. Ojima and N. Inamoto, *Chem. Comm.*, 1970, 1629; (*b*) H. Ulrich, B. Tucker, and A. A. R. Sayigh, *J. Amer. Chem. Soc.*, 1972, **94**, 3484.

[8] H. Ulrich and A. A. R. Sayigh, *Angew. Chem. Internat. Edn.*, 1965, **4**, 520; H. Ulrich, B. Tucker, and A. A. R. Sayigh, *Tetrahedron*, 1966, **22**, 1565.

[9] A. Dondoni, V. Jehlička, and O. Exner, submitted to *Coll. Czech. Chem. Comm.*

least for the cases so far examined, the cycloadditions of carbodi-imides with isothiocyanates appear to attack selectively the two double bonds of the NCS group, the C=S being preferred to the C=N bond.* The 1,3-thiazetidines (3) undergo thermal fragmentation to the starting materials, the equilibrium being favoured from right to left by electron-releasing substituents in R. However, with the exception of (3a) whose cycloreversion to (1a) and DDC was practically quantitative (see below), fragmentation of the other cycloadducts to give minor amounts of scrambled products, *viz.* cyclohexyl isothiocyanate and the corresponding asymmetric carbodi-imide cannot be excluded. The kinetics of the forward and reverse reactions were studied by using *p*-nitrophenyl isothiocyanate (1a) (NPT), DCC, and the corresponding cyclo-adduct (3a). The choice of this system was based on the convenient rates and on the absence of appreciable side reactions, as shown by the identity of the u.v. spectra of equilibrium mixtures obtained from both directions (Table 2). Equilibrium constants (K_e) and rate constants for cycloaddition (k_c) and cycloreversion (k_d) were measured in four solvents at different temperatures; these data, together with the activation parameters calculated therefrom, are recorded in Table 3.

TABLE 1

Some u.v. (cyclohexane) and i.r. (Nujol) data of the 1 : 1 adducts from DCC and isothiocyanates (1)

Isothiocyanate	Adduct λ/nm, (log ε)		Adduct $\nu_{C=N}$/cm^{-1}
(1a)	220 (4.36)	322 (4.30)	1 655
(1b)	212 (4.47)	273 (4.23)	1 655
(1c)	220 (4.35)	270 (4.13)	1 660
(1d)	218 (4.35)	277 (4.17)	1 660
(1e)	218 (4.30)	300 (4.28)	1 660
(1; $R^1 = p$-MeC$_6$H$_4$SO$_2$) [a]	229sh (4.43)		1 620
[1; R^1 = PhP(S)] [a]	223 (4.81)	260sh (4.23)	1 640

[a] Ref. 7*a*.

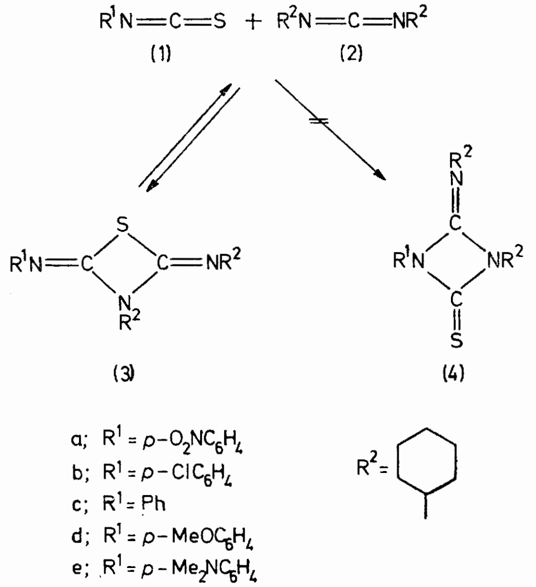

TABLE 2

Absorbances values[a] (A_e) at different wavelengths (λ/nm) of two equilibrium mixtures reached from the opposite directions for the system DCC + NPT $\rightleftharpoons$ (3a) in CH$_3$CN at 50°

Reactant(s) [b]	λ(A_e)	λ(A_e)	λ(A_e)	λ(A_e)	λ(A_e)
DCC + NPT	290 (0.310)	300 (0.420)	310 (0.500)	320 (0.496)	350 (0.120)
(3a)	290 (0.315)	300 (0.420)	310 (0.498)	320 (0.492)	350 (0.120)

[a] After a 250-fold dilution. [b] The initial concentration of each reactant was 0.00653M.

From linear plots of log K_e against $1/T$ the heats of reaction were calculated and showed that the cycloaddition is exothermic by −14 to −19 kcal mol^{-1} in the solvents examined, the values correlating well with those calculated from the differences ($\Delta H_c^{\ddagger} - \Delta H_d^{\ddagger}$). The variations of the equilibrium constants K_e with solvent polarity indicate that the equilibrium of the system is shifted more towards the cycloadduct (3a) in solvents at low dielectric constant, an observation which can be of preparative utility.

The dependence of the reaction rates on the solvent polarity [10] is small since in going from carbon tetrachloride to acetonitrile k_c increases by a factor of two and k_d by a factor ranging between 10 and 20. This rate enhancement as solvent polarity increases is too low to account for the formation of a dipolar intermediate along the reaction co-ordinate whereas it simply indicates that there is a relatively little change in dipole moment at the reacting groups in going from the reactants to transition state to products. On the other hand, well tried trapping experiments [5a,b,6] did not give evidence of the presence of an open-chain intermediate since a mixture of DCC and NPT in liquid sulphur dioxide failed to give an adduct with solvent incorporation but produced only (3a) and a polymer of DCC; moreover, 2 : 1 adducts were not observed when a large excess of one of the reactants was employed. Finally it may be observed that the cycloaddition proceeds in the various solvents with a high negative entropy of activation and a small energy of activation. This is consistent with a tight transition state where redistribution of bonds is mutually assisted. Likewise, the cycloreversion which for the principle of microscopic reversibility must follow the same pathway as the forward process, displays low values of $\Delta S_d^{\ddagger}$, whereas higher values should be expected for the rate-determining formation of open-chain intermediates.[11] All these data, including the selectivity of the cycloaddition, are consistent with a concerted mechanism for

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* An alternate pathway leading to 1,3-thiazetidines (3) is ' by rearrangement of initially formed alternative structures.' Although evidence for the existence of this problem has never been uncovered by several studies on this reaction, the possibility cannot be excluded. This question, raised by one of the referees, remains at present unsolved and should be considered in future work.

[10] R. Reichardt, *Angew. Chem. Internat. Edn.*, 1965, **4**, 29.

[11] J.-M. Vandersavel, G. Smets, and G. L. L'abbé, *J. Org. Chem.*, 1973, **38**, 675.

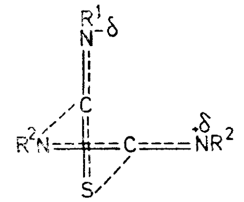
the forward and reverse reactions. For the orbital symmetry requirements of concerted [2 + 2] cycloadditions of cumulenes,[3] the reactants should be arranged orthogonally in the four-centre transition state (5), to allow the orbital overlap in a supra-antarafacial way. However, since the system is not suitable for stereochemical investigations and theoretical treatments are lacking, one cannot safely decide which of the two reactants is the 2_s and which is the 2_a component. By contrast, a clearer point emerges from the observation that the isothiocyanate behaves as an electrophile towards the carbodi-imide, as substantiated by the higher reactivity of isothiocyanates bearing electron-withdrawing groups * (*p*-nitrophenyl, sulphonyl) and the lack of reactivity when, by contrast, these groups are linked to the NCN function.[7b] This substituent effect suggests that bonding between the electrophilic carbon of NPT and the nitrogen of DCC is in advance of formation of the second bond, thus resulting in partial charge separation in the transition state (5).

TABLE 3

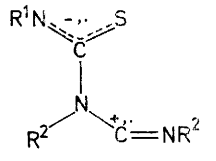
Equilibrium and kinetic data [a] in different solvents [b] for the system DCC + NPT $\underset{k_d}{\overset{k_c}{\rightleftharpoons}}$ (3a)

Solvent	CCl_4			Cyclohexane			Butan-2-one			CH_3CN		
Temp. (°C)	30	50	70	30	50	70	30	50	70	30	50	70
K_e/l mol^{-1}	2 551	269	59.5	2 320	334	70.9	239	45.9	12.5	214	48.1	13.6
10^3k_c/l mol^{-1} s^{-1}	0.359	1.37	5.00	0.40	1.70	4.53	0.493	1.99	5.54	0.670	3.05	12.8 [c]
$10^6k_d/s^{-1}$	0.14 [c]	5.49	100.8	0.17 [c]	5.20	77.6	2.06 [c]	43.0	443	3.13 [c]	62.6	936
$\Delta H_c^‡$/kcal mol^{-1}		12.9			11.9			12.0			14.0	
$\Delta H_d^‡$/kcal mol^{-1}		32.9			30.9			26.9			27.7	
$\Delta S_c^‡$/cal mol^{-1} K^{-1}		−32			−34			−34			−27	
$\Delta S_d^‡$/cal mol^{-1} K^{-1}		+19			+13			+5			+8	

[a] The estimated uncertainties were *ca.* 2% for K_e, 3—4% for k_c and k_d, 0.4 kcal mol^{-1} for $\Delta H^‡$ and 2—3 cal mol^{-1} K^{-1} for $\Delta S^‡$. [b] The molar absorptions of NPT and (3a) at 350 nm in the various solvents were: CCl_4, 1 318, 11 610; cyclohexane, 918, 9 324; butan-2-one, 2 500, 14 050; CH_3CN, 2 920, 14 088. [c] Calculated from K_e and the rate constant of the opposite reaction.



(5)



(6)

Accepting the concept of a concerted reaction mechanism, the energy profile must have a single barrier close to the reactants DCC and NPT to show that the transition state for forming (3a) occurs early along the reaction path since the cycloaddition is an exothermic process. The decrease of $\Delta H_d^‡$ and the constancy of $\Delta H_c^‡$ in going from a non-polar (cyclohexane or carbon tetrachloride) to a polar (butan-2-one or acetonitrile) solvent, may be interpreted in terms of solvation effects † which lower the energy of reactants and transition state to comparable extents whereas that of the adduct remains unaltered.

In conclusion, a scheme where the isothiocyanate–carbodi-imide addition occurs concertedly *via* a four-centre transition state fits the experimental data so far collected. However, as for many other cycloadditions, the distinction between the three mechanisms which are in principle possible, *viz.* dipolar, diradical, or concerted, is far from definitive. In fact, a two-step mechanism cannot be ruled out since its occurrence could be justified by assuming that the intermediate is a short lived species owing to the rapid ring closure through a structure such as (6) which is easily attained by rapid rotation about the central carbon–nitrogen bond. This would account for the difficulty in performing trapping experiments whereas diradical character or a dipole with an internal charge compensation may be responsible for the reduced solvent effect.

EXPERIMENTAL

M. and b.p.s are uncorrected. T.l.c. and column chromatography were done on silica with benzene–light petroleum (1 : 1) as eluant. I.r. spectra were recorded by a Perkin-Elmer 257 grating spectrophotometer and u.v. spectra and absorbances in kinetic and equilibrium experiments were obtained with a Cary 14 spectrophotometer.

Materials.—Solvents were purified by standard procedures.[13] Dicyclohexylcarbodi-imide [14] and aryl isothiocyanates [15] (1a—e) were commercially available or prepared according to standard methods.

General Procedure for the Synthesis of 1,3-*Thiazetidines* (3).—A mixture of aryl isothiocyanate (0.01—0.02 mol) and a 20-fold excess of DCC in CCl_4 (100 ml) was kept at 50° for 16 h and at room temperature for an additional 24 h. The solvent was removed at reduced pressure and the residue was chromatographed to give unchanged isothiocyanate and the cycloadduct. DCC was not recovered since it was partially

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* For *p*-methoxyphenyl isothiocyanate (1d) and DCC in cyclohexane at 50° the following data were obtained: $k_c = 1.03 \times 10^{-5}$ l mol^{-1} s^{-1}; $k_d = 2.80 \times 10^{-6}$ s^{-1}; $K_e = 3.5$ l mol^{-1}.

† Evidence for specific solvation effects by polar solvents on isothiocyanates is based on the shift to higher frequencies of the NCS group [12] [for NPT, $\nu(CCl_4)$ 2 024 cm^{-1}, ν(MeCN) 2 098 cm^{-1}]. Although a detailed i.r. spectral study of (3a) was not carried out, a similar shift of the 1 655 cm^{-1} band was not observed.

[12] Š. Kováč, P. Kristián, and K. Antoš, *Coll. Czech. Chem. Comm.*, 1965, **30**, 3664; L. J. Bellamy, 'Advances in Infrared Group Frequencies,' Methuen, London, 1968, p. 57.

[13] A. Weissberger, 'Technique of Organic Chemistry,' Interscience, New York, 1955, vol. VII.

[14] H. Eilingsfeld, G. Neubauer, M. Seefelder, and H. Weidinger, *Chem. Ber.*, 1964, **97**, 1232.

[15] J. E. Hodgkins and W. Preston Reeves, *J. Org. Chem.*, 1964, **29**, 3098; A. A. R. Sayigh, H. Ulrich, and J. S. Pots, *ibid.*, 1965, **30**, 2465; R. M. Ottenbrite, *J.C.S. Perkin I*, 1972, 88.

polymerized and was not eluted by the solvent adopted. Some u.v. and i.r. data of the adducts are given in Table 1; average yields,[*] m.p.s, and solvent of crystallization (in acetone–solid carbon dioxide) were as follows. 3-Cyclohexyl-4-cyclohexylimino-2-(*p*-nitrophenylimino)-1,3-thiazetidine (3a) (92%) had m.p. 74—75° (from acetone) (lit.,[7b] m.p. 73—75°). 2-(p-*Chlorophenylimino*)-3-*cyclohexyl*-4-*cyclohexylimino*-1,3-*thiazetidine* (3b) was obtained as an oil from the first chromatographic separation and resisted to several attempts of crystallization. Elution of the oily residue with methylene dichloride through a column of silica and treatment with light petroleum induced crystallization (38%), m.p. 68—69° (from methanol) (Found: C, 64.0; H, 6.85; N, 11.1; Cl, 9.5. $C_{20}H_{26}ClN_3S$ requires C, 63.9; H, 6.95; N, 11.2; Cl, 9.45%). 3-*Cyclohexyl*-4-*cyclohexylimino*-2-*phenylimino*-1,3-*thiazetidine* (3c) (55%) had m.p. 75—76° (from light petroleum) (Found: C, 70.4; H, 8.10; N, 12.3; S, 9.25. $C_{20}H_{27}N_3S$ requires C, 70.3; H, 7.95; N, 12.3; S, 9.4%). 3-*Cyclohexyl*-4-*cyclohexylimino*-2-(p-*methoxyphenylimino*)-1,3-*thiazetidine* (3d) was an oil (55%) even after purification from traces of isothiocyanate by elution with light petroleum through a column of silica (Found: C, 67.6; H, 7.85; N, 11.0; S, 8.5. $C_{21}H_{29}N_3OS$ requires C, 67.9; H, 7.85; N, 11.3; S, 8.6%). 3-*Cyclohexyl*-4-*cyclohexylimino*-2-(p-*dimethylaminophenylimino*)-1,3-*thiazetidine* (3e) (31%) had m.p. 67—68° (from light petroleum) (Found: C, 68.7; H, 8.3; N, 14.5; S, 8.3. $C_{22}H_{32}N_4S$ requires C, 68.6; H, 8.4; N, 14.6; S, 8.3%).

Reaction of NPT with DCC in Sulphur Dioxide.—To a solution of DCC (1.9 g, 0.0092 mol) in liquid sulphur dioxide (70 ml) at −78° was added NPT (1.48 g, 0.0082 mol). The reaction flask was equipped with a magnetic stirrer, thermometer, and an acetone–solid carbon dioxide condenser. The solution was allowed to warm to gentle reflux (*ca.* −10°). After 4 h, solvent was removed and the residue chromatographed to yield unchanged NPT (0.69 g, 0.0038 mol) and 1,3-thiazetidine (3a) (1.71 g, 0.0044 mol, 54%); this corresponds to a practically quantitative recovery of (3a). Elution with diethyl ether gave a high melting material, probably a polymer of DCC.

Reaction of DCC with an Excess of NPT.—A solution of DCC (0.46 g, 0.0022 mol) and NPT (2.04 g, 0.011 mol) in carbon tetrachloride (150 ml) was kept at 30° for 4 days. The mixture was worked up by the usual procedure to give NPT (1.57 g, 0.0087 mol) and the 1,3-thiazetidine (3a) (0.84 g, 0.00217 mol, 99%).

Thermolysis of 1,3-*Thiazetidines* (3).—A solution of the selected 1,3-thiazetidine (0.004 mol) in carbon tetrachloride (250 ml) was heated at 50—70° for at least 48 h. The reaction was monitored by t.l.c. and i.r. at 2300 and 2000 cm^{-1} and heating was continued until equilibrium was established as shown by constant i.r. absorbances. The equilibrium mixture was worked up by the usual procedure to yield the aryl isothiocyanate and the unaltered cycloadduct. With the exception of NPT (1a), the isothiocyanates (1b—e) were recovered (80—95% yields) and characterized as benzylthioureas.[16]

Kinetics.—Stock solutions of NPT (1a) and DCC were prepared in the selected solvent at *ca.* 20° and portions (5 ml) were transferred in ampoules which were sealed and placed in a thermostatted bath (± 0.1°). The initial concentrations of NPT were generally in the range 0.0018—0.007M (in CCl_4 at 50° the concentrations were in the range 0.007—0.03M) and those of DCC were at least 15-fold larger. At suitable intervals the ampoules were removed from the bath, cooled in ice–water and an exact amount (2—4 ml) of the solution was diluted to the proper volume with additional solvent. The u.v. absorbance at 350 nm was then measured in matched 10-mm cells with the DCC solution in the reference cell. The initial absorbance A_0 ($t = 0$) and the equilibrium absorbance A_e were obtained from two or three separate determinations. As the measured absorbance A_{tot} is the sum of that of isothiocyanate A_{NPT} and of adduct A_{Ad}, A_{NPT} was calculated from equation (1) where ε_{Ad} and ε_{NPT}

$$A_{NPT} = \frac{A_0\varepsilon_{Ad} - A_{tot}\varepsilon_{NPT}}{\varepsilon_{Ad} - \varepsilon_{NPT}} \qquad (1)$$

are the molar absorptions of adduct (3a) and isothiocyanate respectively; values in the various solvents are given in Table 3. Control experiments showed that at the analytical wavelength the Lambert–Beer law was followed in the range of concentrations employed and from mixtures at known composition of NPT and (3a) it was checked that the A_{NPT} value could be calculated with an error of ± 1%. By plotting the data according to the rate equation for an equilibrium process, first order in both directions,[17a] a good straight line for the log $[(A_{NPT})_t - (A_{NPT})_e]$ against time plot was obtained (subscripts t and e referring to the absorbances of isothiocyanate at time t and at equilibrium respectively) where the slope k_{tot} is the sum $(k_c[DCC]_0 + k_d)$. Hence the linear plot of k_{tot} against $[DCC]_0$ allowed calculation of the rate constant k_c of the forward reaction and provided an indicative value of k_d of the reverse process,

TABLE 4

Rate constants [a] for the cycloaddition of NPT with DCC in various solvents at 50°

Solvent, CH_3CN					
$10^3[NPT]_0/M$	3.86	3.81	4.06	4.01	
$10^2[DCC]_0/M$	4.29	4.35	8.21	12.3	
$10^4k^a_{tot}/s^{-1}$	1.99	1.82	3.17	4.27	
	k_c^b 3.05 × 10^{-3} l mol^{-1} s^{-1}				
Solvent, butan-2-one					
$10^3[NPT]_0/M$	3.60	3.59	3.54	1.79	3.50
$10^2[DCC]_0/M$	4.94	4.97	6.34	11.3	11.6
$10^4k^a_{tot}/s^{-1}$	1.46	1.59	1.87	2.71	2.88
	k_c^b 1.99 × 10^{-3} l mol^{-1} s^{-1}				
Solvent, CCl_4					
$10^3[NPT]_0/M$	7.26	15.5	7.55	40.0	
$10[DCC]_0/M$	1.09	2.00	2.22	0.40	
$10^4k^a_{tot}/s^{-1}$	1.63	2.82	3.13		
10^3k_c/l mol^{-1} s^{-1}				1.60 [c]	
	k_c^b 1.37 × 10^{-3} l mol^{-1} s^{-1}				

[a] Obtained from the integrated plots for first-order reversible processes (see Experimental section) with a standard deviation in duplicate experiments of 3—4%. [b] Obtained from the linear plots of k_{tot} against $[DCC]_0$ ($r \geqslant 0.99$). [c] See ref. 17*b*.

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[*] Yields were calculated with respect to initial isothiocyanate and give only a rough indication of the actual extent of conversion of reactants into product since the amount of the adduct lost during work-up varied in each case (5—15% based on reacted sothiocyanate).

[16] L. E. Weller, C. D. Ball, and H. M. Sell, *J. Amer. Chem. Soc.*, 1952, **74**, 1104; S. P. Kharida, P. R. Pathan, P. S. Satpanthi, and J. J. Trivedi, *J. Indian Chem. Soc.*, 1960, **37**, 705 (*Chem. Abs.*, 1961, **55**, 10,372f); K. N. Campbell, B. K. Campbell, and S. J. Patelski, *Proc. Indiana Acad. Sci.*, 1943, **53**, 119 (*Chem. Abs.*, 1945, **39**, 881); F. Zetzsche and A. Fredrich, *Ber.*, 1940, **73**, 1114 (*Chem. Abs.*, 1941, **35**, 2480h).

[17] (*a*) A. A. Frost and R. G. Pearson, 'Kinetics and Mechanism,' Wiley, New York, 1967, p. 186; (*b*) C. Capellos and B. H. J. Bielski, 'Kinetic Systems,' Wiley–Interscience, New York, 1972, p. 43.

which was very close to that obtained from independent experiments starting from (3a) (see below). In some runs the initial concentrations of NPT and DCC were identical and the k_c values calculated by the appropriate equation [17b] were consistent with those obtained as described above.

The same procedure was employed for the determination of the rates of cycloreversion. The initial concentrations of (3a) were in the range 0.0008—0.006M. The rate constants k_d were calculated from the equation [17] for an equilibrium process involving a first-order forward reaction and a second-order reverse reaction.

The rate constants obeyed the Arrhenius equation and the activation parameters were evaluated by standard methods.[18]

Determination of Equilibrium Constants.—Four or five solutions of (3a) in the selected solvent with concentrations variable from 0.001 to 0.015M were allowed to equilibrate in sealed ampoules at the appropriate temperature. The equilibrium concentrations of the reactants were determined from the 350 nm u.v. absorbances at equilibrium (A_e) and at time $t = 0$ (A_0), as well as from the molar absorptions ε_{Ad} and ε_{NPT}. The K_e values listed in Table 3 were calculated by the usual equation and refer to the equilibrium formation of the adduct (3a).

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[18] S. Glasstone, K. J. Laidler, and H. Eyring, ' The Theory of Rate Processes,' McGraw-Hill, New York, 1941, ch. 6.