Concentration Dependence of the Rate Constants for $2+2$ Cycloadditions of Tetracyanoethylene

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Summary The dependence of the second-order rate constants for the $2+2$ cycloaddition of tetracyanoethylene to dihydropyran on the molar concentration in various solvents is due to a change in the polarity of the medium rather than to variation in charge-transfer complex concentration.

The dependence of a rate constant on the concentration of a reactant appears paradoxical and usually indicates that the reaction order was incorrectly assumed. In the Diels-Alder reaction of 9,10-dimethylanthracene with maleic anhydride or chloromaleic anhydride in chloroform, a decreasing k_2 with increase of the dienophile concentration was interpreted by Andrews and Keefer[1] as evidence for reaction within the charge-transfer (CT) complex or a kinetically indistinguishable combination of uncomplexed reactants.

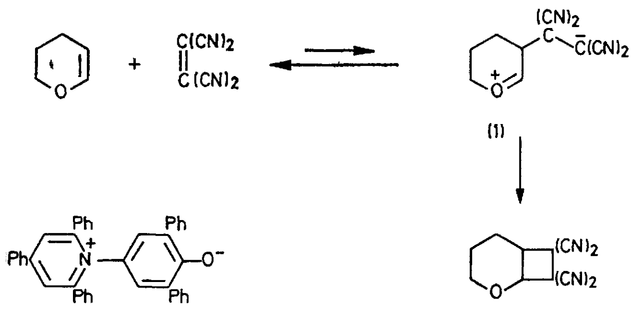
The rate of cyclobutane formation from tetracyanoethylene (TCNE) and enol ethers can be measured photometrically by the disappearance of the colour of the CT complex.[2,3] The fading of the red colour of a solution of TCNE and a large excess of dihydropyran follows the first-order law. Division of the pseudofirst-order rate constant by the molar concentration of dihydropyran provides the overall second-order rate constant k_2 which depends on the concentration of the enol ether and the nature of the solvent (Table).

Table

Rate constants for the $2+2$ cycloadditions of TCNE (0·003—0·012 M) to 3,4-dihydro-2*H*-pyran and $E_{\rm T}$ values for various mixtures of dihydropyran with solvent

Solvent	Dihydropyran M	Dihydropyran % weight	$10^3 k_1$ /sec^{-1}	$10^3 k_2$ /l mol^{-1} sec^{-1}	$E_{\rm T}$ /kcal mol^{-1}
Acetonitrile	0·438	4·73	3·19	7·28	45·5
	2·20	22·8	11·9	5·40	44·7
	6·08	59·3	8·11	1·33	42·8
	8·81	82·5	3·29	0·373	40·8
	10·11	93·2	1·17	0·115	39·0
	10·52	95·6	0·604	0·0574	37·9
	10·96	100	0·200	0·0182	36·0
Dioxan	0·557	4·62	0·00853	0·0153	36·0
	4·63	39·6	0·0745	0·0161	36·0
	7·68	67·0	0·134	0·0175	36·0
	10·96	100	0·200	0·0182	36·0
Di-n-butyl ether	0·547	5·98	0·00112	0·00205	33·4
	2·17	23·0	0·00784	0·00361	34·0
	4·39	44·6	0·0245	0·00558	34·6
	7·64	74·0	0·127	0·0166	35·6

In acetonitrile, k_2 is diminished 400 fold by changing successively the dihydropyran concentration from 0·44 M (4·7%) to 11 M (100%). In contrast, in dioxan as solvent the concentration dependence is negligible. In dibutyl ether, however, k_2 increases 9 fold in going from a 0·55 M (6·0%) to a 11 M solution of dihydropyran. Wiley[4] observed in the system TCNE + *p*-methoxystyrene (from 0·05 to 0·20 M) a small decrease of k_2 in nitromethane and in acetonitrile and a 1·7 fold increase in toluene.



(1)

(2)

The 2+2 cycloadditions of TCNE to enol ethers take place *via* a reversibly formed zwitterion (**1**), shown by the lack of stereospecificity,[5] the geometrical isomerisation of *cis-trans* isomeric enol ethers,[5] the structure-rate correlation[3] the pressure dependence of rate,[6] and the trapping reaction with alcohols.[7] The rate constant depends highly on solvent polarity, *e.g.*, TCNE adds to dihydropyran in acetonitrile 17,000 times faster than in CCl_4.[2] The log k_2 values in various solvents are a linear function of E_T, an empirical parameter of solvent polarity,[8] based on the solvatochromism of (**2**).

We suspected that the dependence of k_2 on the dihydropyran concentration might be due to the polarity change of the medium. Therefore, we determined E_T values spectroscopically for the same solutions of dihydropyran in acetonitrile, dioxan and dibutyl ether which were used for the kinetic measurements of TCNE cycloadditions (Table). All the log k_2 values give an excellent straight line when plotted *vs.* the E_T of the mixtures (slope = 0·287). Pure dihydropyran shows E_T = 36·0 kcal mol^{-1}, much lower than that of acetonitrile (46·0), identical with the dioxan value, and slightly larger than E_T of dibutyl ether (33·4). This explains the magnitude and direction of the concentration dependence of k_2 as an effect of solvent polarity. The lack of a deviation from linearity shows that CT complex formation of TCNE with enol ether does not affect the rate.

Though the concerted Diels-Alder reaction displays a much smaller solvent dependence than the 2+2 cycloaddition dealt with here, our results make a re-investigation of the system dimethylanthracene + maleic anhydride desirable, especially so since in acetone as solvent no decrease of k_2 with increasing dienophile concentration was observed.[1]

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