KINETICS OF [2+2] CYCLOADDITIONS OF 2,2-BIS(TRIFLUOROMETHYL)ETHYLENE-1,1-DICARBONITRILE WITH ENOL ETHERS, 1,1-DIMETHYLBUTADIENE, AND ALLYLTRIMETHYLSILANE [1]

Reinhard Brückner and Rolf Huisgen[*]

Institut für Organische Chemie der Universität München

Karlstr. 23, 8000 München 2, West Germany

Summary: The rate constant with ethyl vinyl ether is enhanced by α-donor substitutents whereas β-methyl groups strongly retard by steric hindrance. The title compound (BTF) is 2400 times more active than TCNE towards ethyl vinyl ether in benzene. The rates of the title reactions increase 70- to 2300-fold with solvent polarity.

We established previously that electron-deficient olefins like tetracyanoethylene (TCNE) combine with donor-substituted ethylenes forming cyclobutanes **2** via zwitterions **1** [2]. Monitoring spectrophotometrically the decay of the charge transfer absorption of the reactants (≥ 10 equiv. of donor olefin) provided second-order rate constants [3]
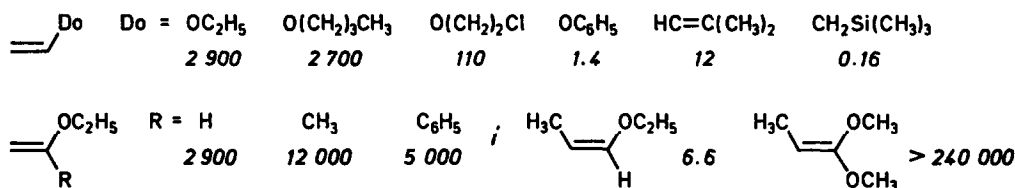
$$k_2 = k_i \cdot k_c/(k_c + k_{-i}).$$

Neglect of the partition coefficients (0.5 - 1 for TCNE, 0.87 - 1 for BTF) allowed regarding k_2 as a measure of k_i, the zwitterion formation. Comparison with Diels-Alder rates strongly suggested late, i.e., zwitterion-like transition states for the [2+2] cycloadditions of polycyanoethylenes with donor olefins [4]. Thus, observed k_2 values approximate energy differences of ground state and zwitterion.

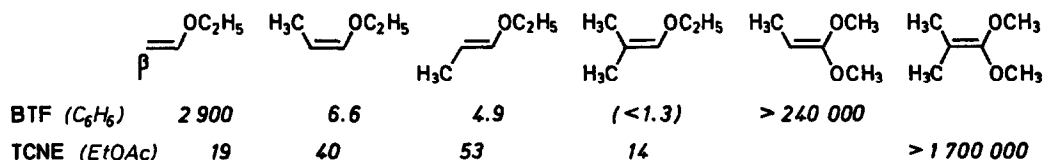|			ΔH_r for Do = OBu
A = CN TCNE	1	2	$(CH_2Cl_2, 25°C)$
A = CF$_3$ BTF	3	4	-22.0 kcal mol^{-1}
			-27.1 "
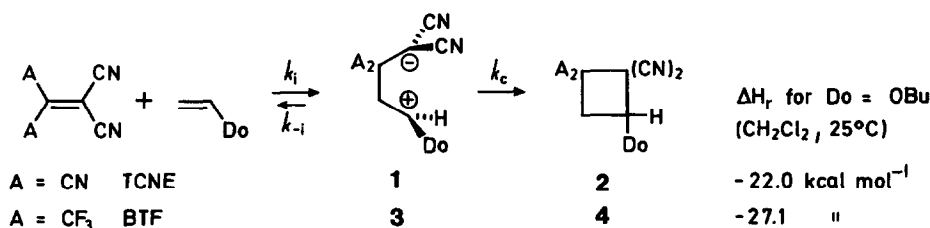
In 1965, Middleton reported the "almost instantaneous" cyclobutane formation from enol ethers and 2,2-bis(trifluoromethyl)ethylene-1,1-dicarbonitrile (BTF) [5]. Here we substantiate this notion *quantitatively*. Chemical and stereochemical evidence for the intermediacy of 1,4-dipoles **3** in [2+2] cycloadditions of BTF has been presented [6]. The consumption of starting materials was determined photometrically as above. All numerical data below the formulae refer to $10^3 k_2$ (M^{-1}s^{-1}) in benzene at 25°C.

The electron-donating capacity (+M effect) of the oxygen in ethyl vinyl ether is reduced in the chloroethyl and phenyl vinyl ether; the 26- and 2000-fold decrease of k_2 mirrors the stabilization of
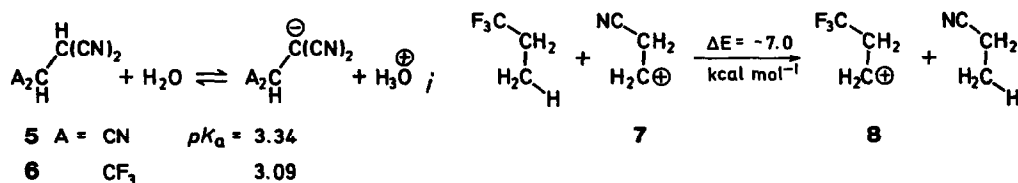
the carboxonium ion in **3**. The lower k_2 for Do = dimethylvinyl and $CH_2Si(CH_3)_3$ indicate that stabilization by allyl and β-silicon function is inferior to that by carboxonium. The rate increase of ethyl vinyl ether by α-methyl is 4-fold and by α-phenyl only 1.7-fold, due to lack of planarity; only part of the benzyl cation resonance becomes effective in **3**. The tremendous rate increase by a second ether function was measured for 1,1-dimethoxypropene.

	Do =	OC_2H_5	$O(CH_2)_3CH_3$	$O(CH_2)_2Cl$	OC_6H_5	$HC=C(CH_3)_2$	$CH_2Si(CH_3)_3$
		2 900	2 700	110	1.4	12	0.16

	R = H	CH_3	C_6H_5			
	2 900	12 000	5 000	6.6		> 240 000

The small influence of the first and second β-CH_3 group on the cycloaddition rate of ethyl vinyl ether with TCNE [$10^3\ k_2$ ($M^{-1}s^{-1}$), ethyl acetate, 25°C] [3] suggests a compensation of electronic activation and steric hindrance. The latter dominates for BTF; k_{BTF} for ethyl vinyl ether plunges 440- and 590-fold on introduction of *cis-* or *trans-*CH_3. For BTF + isobutenyl ethyl ether, the [2+2] cycloaddition is suppressed in favor of a slow hydride transfer [7]. The massive steric effect is due to the bulky CF_3 groups: conformational A value 2.4-2.5 kcal mol^{-1} for CF_3 [8] vs. 0.17 kcal mol^{-1} for the slim CN group [9].

	OC_2H_5	H_3C OC_2H_5	OC_2H_5 H_3C	H_3C OC_2H_5 H_3C	H_3C OCH_3	H_3C OCH_3 H_3C OCH_3
BTF (C_6H_6)	2 900	6.6	4.9	(<1.3)	> 240 000	
TCNE $(EtOAc)$	19	40	53	14		> 1 700 000

Since the CF_3 groups are located at a C_q of zwitterion **1**, it is not even sure that k_2 of BTF + vinyl ether is void of steric effects. The more impressive is the superiority of BTF over TCNE: k_{BTF}/k_{TCNE} for butyl vinyl ether amounts to 2400 in benzene ($\Delta\Delta G^{\neq}$ 4.6 kcal mol^{-1}) and 190 in ethyl acetate at 25°C ! This stunning difference might arise from two effects: greater stability of zwitterion **3** vs. **1** and diminished stability of BTF vs. TCNE.

$$A_2C \overset{H}{\underset{H}{\big|}} C(CN)_2 + H_2O \rightleftharpoons A_2C \overset{\ominus}{\underset{H}{\big|}} C(CN)_2 + H_3O^{\oplus}$$

$$F_3C{\diagdown}{CH_2} + NC{\diagdown}{CH_2} \xrightarrow[\text{kcal mol}^{-1}]{\Delta E = -7.0} F_3C{\diagdown}{CH_2} + NC{\diagdown}{CH_2}$$

5 A = CN	pK_a = 3.34	**7**
6 CF_3	3.09	**8**

Concerning zwitterion stabilities, the expectation that the greater -I effect - Taft's σ_1 is 0.57 for CN vs. 0.40 for CF_3 - makes **1** more stable than **3** is not borne out by potentiometric titration [10]: two CF_3 groups in **6** acidify the malononitrile group slightly more than two CN in **5**. The effect of CN vs. CF_3

on the cationic moiety of the zwitterion appears to be greater. According to calculations on the STO-3G level, the isodesmic reaction involving **7** and **8** is exothermic and indicates a destabilization by γ-CF_3 < γ-CN [11].

BTF is probably *less* stable than TCNE compared with the corresponding [2+2] cycloadducts. We found the enthalpy of the cycloaddition of butyl vinyl ether with BTF by 5.1 kcal mol^{-1} more exothermic than that with TCNE [12] (see above) which exceeds somewhat the expectation for the loss of conjugation energy of two CN in TCNE. Considering the late transition state of zwitterion formation, the higher electron affinity of BTF vs. TCNE [13] - anyway surprising - as a measure of LU energy should be less important.

Solvent effects on the rate constant reflect different solvation of starting materials and transition state. When educts of *little* polarity furnish a zwitterion with separated formal charges, a strong increase of polarity in the activation step is expected. The [2+2] cycloaddition of ethyl isobutenyl ether (dipole moment μ = 1.28 D) and TCNE (μ zero) proceeds in acetonitrile 10 800 times faster than in cyclohexane; μ = 17 D was estimated for the gauche zwitterion of type **1**, and the cyclobutane of type **2** showed μ = 6.05 D [14]. The mentioned rate ratio reached even 29 000 for anethole + TCNE. Values of log k_2 in many solvents entertained fairly linear relations with E_T, Reichardt's empirical parameter of solvent polarity [15].
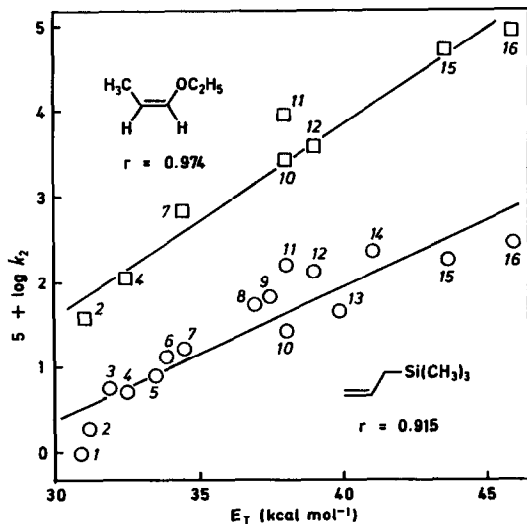

Figure 1. Plots of log k_2 for [2+2] cycloadditions of BTF to ethyl *cis*-propenyl ether and allyltrimethylsilane vs. E_T. Solvents: *1* hexane, *2* cyclohexane, *3* $Cl_2C=CCl_2$, *4* CCl_4, *5* *p*-xylene, *6* toluene, *7* benzene, *8* *m*-$C_6H_4Cl_2$, *9* C_6H_5Cl, *10* *o*-$C_6H_4Cl_2$, *11* ethyl acetate, *12* $CHCl_3$, *13* methyl acetate, *14* CH_2Cl_2, *15* propionitrile, *16* acetonitrile.

We measured μ = 1.74 D (benzene, 25°C) for BTF; thus, the [2+2] cycloaddition starts with a higher level of polarity. The polarity of the zwitterion **3** may be somewhat lower than for **1**, since μ = 4.84 D was found for the cyclobutane from BTF and ethyl *trans*-propenyl ether. Accordingly, the k_2 of BTF were less sensitive to solvent polarity than those of TCNE. Ratios of k values in acetonitrile and cyclohexane amounted to 70 for 1,1-dimethylbutadiene and β-chloroethyl vinyl ether, 160 for allyltrimethylsilane, 170 for butyl vinyl ether, and 2300 for ethyl *cis*-propenyl ether. The linearity of the log k_2/E_T plots, illustrated by two examples in Fig. 1, is less well fulfilled than for the TCNE data.

REFERENCES AND NOTES

1. *Dedicated to Professor Paul von R. Schleyer, Erlangen, on the occasion of his sixtieth birthday.*

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12. We thank Professor R. *Wachter*, University of Regensburg, for making his microcalorimeter available to us.

13. One-electron reduction potentials in acetonitrile / $LiClO_4$ vs. Ag/AgCl at 25°C. Pt cathode: BTF -0.07 V, TCNE -0.39 V; glassicarbon cathode: BTF -0.06 V, TCNE -0.37 V. We are grateful to Professor S. *Hünig*, University of Würzburg, for kindly carrying out these measurements.

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