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HETERODIENE SYNTHESES—XXV[1]

KINETICS OF THE REACTION OF ETHOXYETHENES WITH 1-PHENYL-4-BENZYLIDEN-5-PYRAZOLONE. ACTIVATION ENERGIES VS. ENERGY GAINED IN THE CYCLOADDITION.†

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Abstract—The kinetics of the reaction between 1-phenyl-4-benzyliden-5-pyrazolone and ethoxyethenes have been studied by quantitative spectroscopic analysis in xylene at various temperatures.

These 1,4-cycloadditions are HOMO-ethoxyethene controlled but Sustmann's approximation of the general perturbation equation cannot be used to rationalize the results since meaningless relationships are obtained by plotting the log of the rate constants vs the inverse of ethoxyethene HOMO energies.

If the energy gained in the cycloaddition, calculated by MO energies and coefficients, is plotted vs the log of the rate constants a good relationship is obtained which results better if the entropy factor is excluded.

In previous papers[2-4] we have investigated the effect of substituents on the rate of the 1,4-cycloaddition between 4-aryliden-5-pyrazolones and alkyl vinyl ethers (Scheme 1)

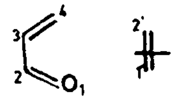
Whereas in position 3 alone the substituent R has no effect on the rate,[2] by varying other substituents the following results have been obtained:

(a) The substituent X on the 1-aryl group increases the rate of the reaction with its electron-attracting character and a correlation is obtained between log k and σ constants.[3]

(b) The substituent Y on the 4-aryliden group increases the rate with its electron-attracting character and a correlation is obtained with σ^+ constants.[4]

(c) The substituent Z on the vinyl ether increases the rate with its electron-donating character and a correlation is obtained with σ^* constants.[2,4]

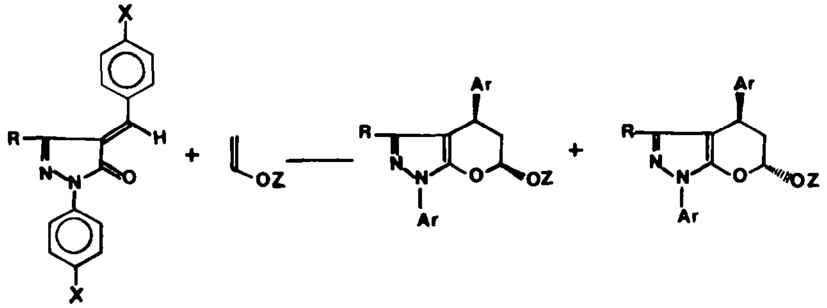
All these data can be rationalized if the reaction is considered to be frontier-controlled with a dominant interaction between pyrazolone LUMO and vinyl ether HOMO. The second order energy change for a Diels-Alder reaction of the type



is given by eqn (1)

$$E = 2\beta^2\left[\frac{(C^{1}_{HO}C^{1'}_{LU}+C^{4}_{HO}C^{2'}_{LU})^2}{E^{diene}_{HO}-E^{dienoph}_{LU}-Q}\right] + 2\beta^2\left[\frac{(C^{1'}_{HO}C^{1}_{LU}+C^{2'}_{HO}C^{4}_{LU})^2}{E^{dienoph}_{HO}-E^{diene}_{LU}-Q}\right]. \quad (1)$$

It incorporates the delocalization term with the denominator lowered by a factor Q which represents the coulombian attraction between the positively charged donor and the negatively charged acceptor[5]. Under the



Scheme 1.

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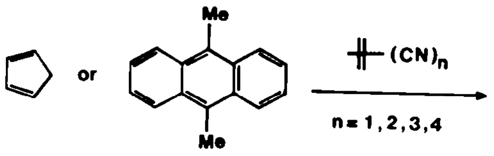
Sustmann's approximation,[6] i.e. the contribution from the eigenvector coefficients assumed to be constant, eqn (1) is simplified to eqn (2)

$$\Delta E = 2\beta^2\left[\frac{1}{E_{HO}^{diene} - E_{LU}^{dienoph} - Q}\right] + 2\beta^2\left[\frac{1}{E_{HO}^{dienoph} - E_{LU}^{diene} - Q}\right]. \qquad (2)$$

If the first term is negligible and substituents coefficients (σ, σ^+ or σ^*) are simply a measure of the variation of pyrazolone LUMO (σ and σ^+) or of vinyl ether HOMO (σ^*) a linear dependence is obtained since a portion of the hyperbolae branch represented by the simplified eqn (2) is involved. This was strongly supported by a good correlation between the kinetic date and the polarographic one-electron half-wave reduction potentials,[3] which represent an experimental measure of the relative energy of the LUMOs.

The reaction of cyclopentadiene or dimethylanthracene with cyanoethenes[6a,7] can be rationalized in a similar fashion. The reactions obviously are HOMO diene—LUMO dienophile controlled[5] and good linear relationships are obtained by plotting log K vs 1/E.A. cyanoethenes (Scheme 2).

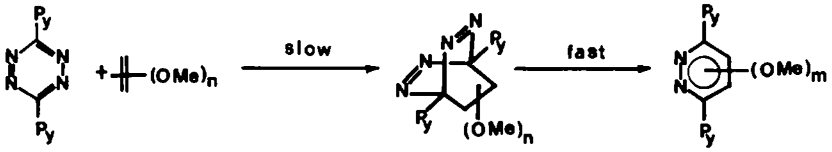


Scheme 2.

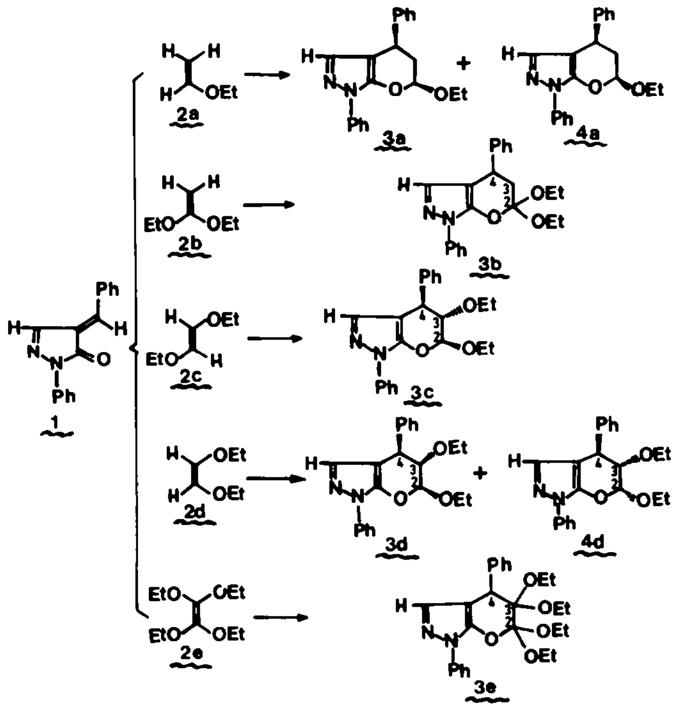
Unfortunately this approach cannot be generally applied since if the rate constants of the reaction of 3,6-di(2-pyridil)s-tetrazine and methoxyethenes[8] (Scheme 3) are plotted vs 1/I.P.methoxyethenes meaningless results are obtained.

In this paper we wish to discuss the kinetic data of the reaction between 1-phenyl-4-benzal-5-pyrazolone (**1**) and ethoxyethenes: ethyl vinyl ether (**2a**), 1,1-diethoxyethene (**2b**), E-1,2-diethoxyethene (**2c**), Z-1,2-diethoxyethene (**2d**) and 1,1,2,2-tetraethoxyethene (**2e**). Some of the starting vinyl ethers are commercial products, some of them are easy to be obtained, **2c** and **2d** are tedious to be prepared but much more tedious to be isolated as pure materials since a repeated preparative gas-chromatographic separation is required (Experimental).

Both under the kinetic conditions and in the presence of excess vinyl ether as solvent, **1** reacted with each vinyl ether in accordance with a 1,4-cycloaddition only and a single adduct ((**3b**, **3c** and **3e**), or two adducts (**3a,d** and **4a,d**) were obtained whose configuration was deduced by NMR. The overall behaviour is reported in Scheme 4 and the details of preparations, separations and structure determinations are reported in the Experimental.



Scheme 3.



Scheme 4.

RESULTS AND DISCUSSION

The kinetic runs were studied in xylene at different temperatures and followed to 60–80% completion by quantitative spectroscopic analysis following the disappearance of the starting pyrazolone **1** at 328 nm (Experimental).

The reactions were shown to be second-order, first-order with respect to each reagent;[3] a 100/500 fold molar excess of vinyl ether gave pseudo-first-order conditions and rate constants, measured under these conditions, as well as the thermodynamic parameters of each reaction, are shown in Table 1.

At 63.5° all vinyl ethers gave measurable rates, thus if the slower reaction is taken as a reference, the relative rates can be obtained (Table 2).

The order of reactivity is **2d** < **2e** < **2c** < **2a** ≪ **2b**, which does not follow the order of the ionization potentials (Table 2), since the faster reaction occurs with 1,1-diethoxyethene whereas the lower I.P. is that of 1,1,2,2-tetraethoxyethene. Simple substituents considerations would bring a similar result.

Thus, taking into account that the reaction is HOMO ethoxyethene—LUMO pyrazolone controlled, under the conditions of the Sustmann's approximation, only the first term of eqn (2) has to be considered. Since the energy of the LUMO of pyrazolone is a constant, a linear dependence should be obtained by plotting log k at 63.5° vs 1/I.P. When this was done, meaningless results were obtained (Fig. 1) thus suggesting either that the reaction is not under frontier control or that the Sustmann's approximation cannot be adopted for ethoxyethenes.

Since we were convinced of our original approach, we calculated the energy gained in the cycloaddition (ΔE) for the model reaction between acrolein and ethoxyethenes using the LUMO energy and coefficients for acrolein taken from the literature,[9] ($E_{LUMO} = 0$ eV; $C^1_{LUMO} = 0.51$; $C^4_{LUMO} = 0.59$). Furthermore the HOMO energies of ethoxyethenes can be given by the negative of their I.P.s (Table 2) and the HOMO coefficients for

Table 2. Relative rates for the reaction of **1** with ethoxyethenes in xylene at 63.5° and I.P.s of ethoxyethenes

Ethoxyethenes	k_{rel}	-I.P.(ev)
2d	1	8.15[a]
2e	15	7.89[b]
2c	27	8.23[a]
2a	57	8.95[a]
2b	47.700	8.30[a]

a)Taken from ref.8. b)P.Colonna, personal communication

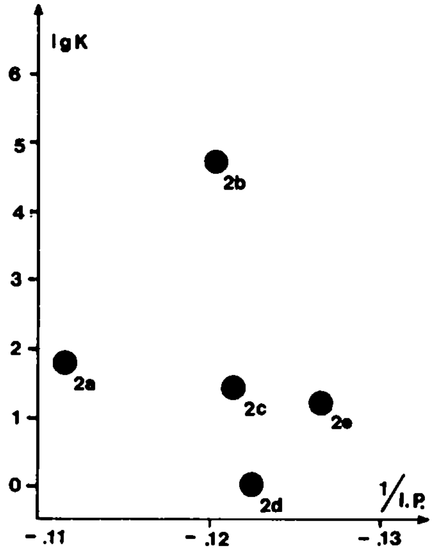
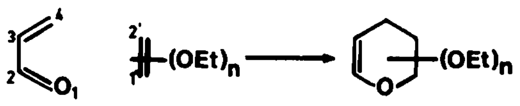


Fig. 1. Plot of log k vs 1/I.P. (ethoxyethene) in the reaction of **1** and **2** in xylene at 63.5.

Table 1. Rate constants and thermodynamic parameters for the reactions of **1** and ethoxyethenes

Temp. (°C)	Ethoxyethenes **2a**	**2b**	**2c**	**2d**	**2e**
17.5	--	$3.27.10^{-2}$ ±0.09	--	--	--
29.5	--	$6.16.10^{-2}$ ±0.20	--	--	--
40.5	$4.65.10^{-5}$ ±0.25	$1.00.10^{-1}$ ±0.08	$3.17.10^{-5}$ ±0.12	--	$2.48.10^{-5}$ ±0.22
50.2	--	$1.24.10^{-1}$ ±0.07	--	--	--
63.5	$2.86.10^{-4}$ ±0.09	$2.41.10^{-1}$ ±0.15	$1.36.10^{-4}$ ±0.09	$5.05.10^{-6}$ ±0.15	$7.65.10^{-5}$ ±0.19
80.2	--	--	--	$1.31.10^{-5}$ ±0.18	--
95.2	$1.30.10^{-3}$ ±0.09	--	$8.12.10^{-4}$ ±0.18	$3.35.10^{-5}$ ±0.24	$5.76.10^{-4}$ ±0.22
$\Delta E^{\neq}$ (Kcal/mol)	13.7 ±0.5	8.1 ±0.5	13.4 ±0.3	14.4 ±0.8	13.1 ±0.5
$\Delta S^{\neq}$ (e.u.)	-37 ±1.5	-39 ±1.2	-39 ±1.0	-42 ±2.2	-40 ±1.5

Table 3. HOMO coefficients and E/β^2 values for the reaction of ethoxyethenes (**2a–e**) and acrolein



2	HOMO coefficients (CNDO/2)[a]		E/ ^{2}
	$c^{1'}$	$c^{2'}$	
a	0.405	0.631	0.1126
b	0.378	0.709	0.1409
c	0.496	0.496	0.1138
d	0.483	0.483	0.1096
e	0.499	0.499	0.1217

a) Calculated for methoxyethenes.

2a–d were calculated with the CNDO/2 method by Houk[10] for the corresponding methoxy derivatives. Those for **2e** we calculated (for the tetramethoxy-derivative also) by the same method under conditions of optimization of the binding energy.

Thus we have reported in Table 3 the HOMO coefficients and the values of $\Delta E/\beta^2$ obtained by eqn (1) from its first term only.

Of the several possibilities for Q, which is the factor correcting the denominator for the electrostatic attraction of the reagent donor, with the reagent acceptor giving rise to a change transfer, best results in the correlations (*vide infra*) were obtained if the value of 4–5 eV, suggested by Houk[11] for point charges interaction, is lowered to 3 eV which is certainly consistent for molecules with largely delocalized charges.

If we plot log k (at 63.5°) vs $\Delta E/\beta^2$ a reasonable result is obtained (Fig. 2a) with a tendency to the linearity which can be appreciated if Fig. 2(a) is compared with Fig. 1.

But ΔE (the energy gained in the cycloaddition) taken from eqn (1), is the energy gained when the orbitals of one reagent overlap those of the other and when we compare ΔE vs log k, since $\log k = -\Delta G/RT$, we assume a direct proportionality between the energy gained and the free energy (Eqn (3)).

$$\Delta E = a \log k = b\Delta G. \tag{3}$$

To assume this means to consider both the enthalpy and the entropy contribution since ΔG is equal to $\Delta H - T\Delta S$. Thus a factor, the entropy, is taken into account which is not involved in frontier molecular orbitals interaction.

Since with the perturbation approach we do get an estimate of the *slope* of an early part of the path along the reaction coordinate leading up to the *transition state*, a correlation is conceivable between the perturbation energy (ΔE) and the activation energy ($\Delta E^{\neq}$) (eqn 4).

$$\Delta E = c.\Delta E^{\neq} + k. \tag{4}$$

Thus to fulfill eqn (4) we have plotted the experimental activation energies of the reaction of **1** with **2a–e** (Table 1) vs calculated $\Delta E/\beta^2$ values (Table 3) and the result is shown in Fig. 2(b).

FINAL CONSIDERATIONS

The correlations obtained in Fig. 2 clearly demonstrate a frontier control of the reaction with a dominant interaction between HOMO ethoxyethene and LUMO pyrazolone. This is in general not difficult to predict for a cycloaddition by a simple comparison between substituents effect and reactivity. What we point out with our results is that Sustmann's approximation of the perturbation equation (i.e. eqn 2) must be used with great care.

For electron-deficient olefins (e.g. cyanoethenes) the olefin LUMO control of the cycloadditions (Scheme 2) is

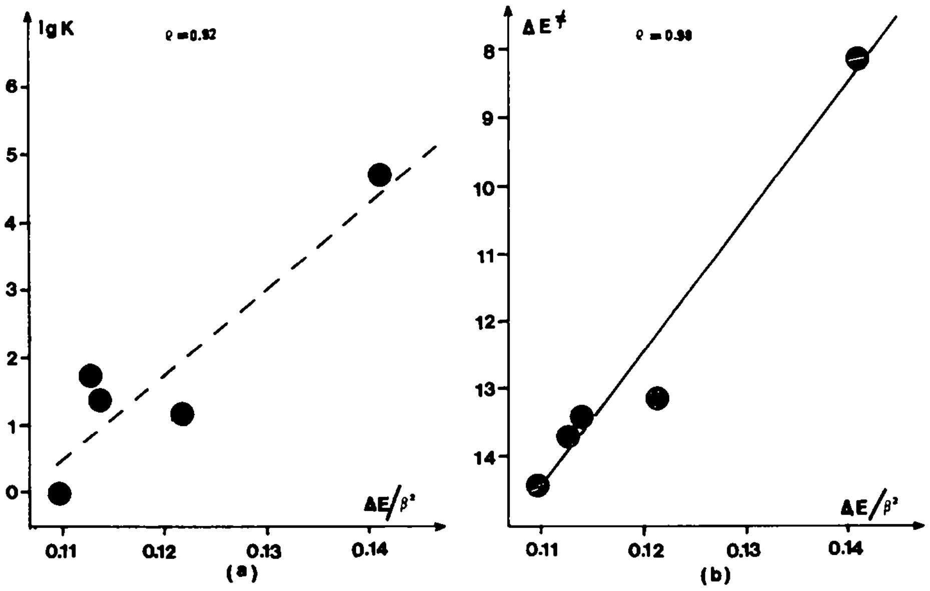


Fig. 2. Plot of the calculated E/β^2 values vs log k (at 63.5): (a) and vs the activation energies (b) of the reaction of pyrazolone **1** and ethoxyethanes (**2a–e**).

a favourable situation. Its coefficients are weakly polarized (acrylonitrile has $C_1^{LU} = -0.54$ and $C_2^{LU} = 0.66$)[5b] and their value is not significantly affected by number and position of substituents. Hence the numerator of eqn (1) (first term) can be taken as a constant.

For electron-rich olefins the HOMO coefficients are strongly polarized (1-aminoethene has $C_1^{HO} = 0.20$ and $C_2^{HO} = 0.50$),[5b] hence to consider that coefficients of asymmetrically- and symmetrically-substituted ethenes are constant is an unacceptable assumption.

The observed relationship between calculated energies and energies of activation is predicted by theory and is nicely supported by the experimental observation. Deviations are probably rationalized for overcrowded molecules in terms of steric effects which can induce conformational changes within the series.

EXPERIMENTAL

IR spectra (Nujol mulls) were obtained with a Perkin Elmer 257 spectrophotometer. NMR data were obtained by Prof. Anna Gamba Invernizzi with a Perkin Elmer R 12A spectrometer (solvent $CDCl_3$, TMS as internal standard). Microanalyses were performed by Dr. Lucia Maggi Dacrema. M.ps. are uncorrected.

Compound 1 was prepared in accordance with the literature method.[12]

2a was redistilled Erba reagent; **2b** was prepared in accordance with the lit. method[13] and compound **2c** was prepared in admixture with **2d** according to the lit. method.[14,15] After carefull purification by distillation, a mixture of **2c** and **2d** was obtained (b.p. 133–134°) which was shown gas chromatographically (Carbowax 20 M 10% on Cromosorb W-100°–N_2 flow 0.2 kg/cm^2) to be in the ratio 65:35. **2c** was carefully purified, as well as **2d**, from the above mentioned mixture by double preparative gaschromatography with the following conditions: Gaschromatograph: Erba GT; column: Carbowax 20 M 20% (200 cm); column temp.: 100°; nitrogen flow: 0.28 kg/cm^2; inlet temp.: 160°; detector temp.: 160°; **2c**: retention time 40′; **2d**: retention time 48′.

The compounds thus obtained were purified with a second gaschromatographic preparation. Pure samples thus obtained have amounts of the second isomer at a concentration lower than 0.1%.

Compound **2d** was obtained as above described and **2e** was prepared in accordance with the lit. method.[16–18]

Reaction of 1 with **2a** was performed as described in Ref. 4. 78% yield of **3a** and 22% of **4a** were obtained.

Reaction of 1 *with* **2b**. A mixture of 1 (2 mmoles) and **2b** (10 mmoles) was allowed to react at room temp. Within a few minutes the red colour of 1 disappeared and colourless crystals of **3b** separated in quantitative yield m.p. 158–159° (cyclohexane). IR: no band in the CO region. NMR: ABX spectrum for H_3, $H_{3'}$ and H_4 protons at 2.07, 2.38 and 4.06δ respectively; OCH_2 at 3.74q, CH_3 at 1.14 t and 1.23 tδ (Found: C, 72.66; H, 6.73; N, 7.63 Calc. for $C_{22}H_{24}N_2O_3$: C, 72.50; H, 6.64; N, 7.69%).

Reaction of 1 *with* **2c**. A mixture of 1 (2 mmoles) and **2c** (8 mmoles) was allowed to react in a sealed tube at 100° for 24 hr. The excess **2c** was evaporated from the light amber coloured soln where TLC showed the presence of a single product. When crystallized from EtOH/H_2O, white crystals of **3c** were obtained in nearly quantitative yield; m.p. 97–98°. IR: no band in the CO region. NMRδ H_2, H_3 and H_4 at 5.28 d, 3.62 dd and 4.02 d respectively ($J_{2,3} = 5.65$ and $J_{3,4} = 6.45$ Hz); OCH_2 at 6.24 q, OCH_2 at 3.41 dq and 3.71 dq, CH_3 at 1.01 t and 1.20 t. (Found. C, 72.64; H, 6.77; N, 7.51. Calc for $C_{22}H_{24}N_2O_3$: C, 72.50; H, 6.64; N, 7.69%).

Reaction of 1 *with* **2d**. A mixture of 1 (0.5 mmoles) and **2d** (1 mmol) was allowed to react in a sealed tube at 100° for 5 days. A few drops of EtOH were added to the light brown oil and soft white needles of **3d** separated. The mother liquors were chromatographed (Silicagel H Merk, cyclohexane/EtOAc 95:5) and two fractions were eluted, the second one being a further crop of **3d**, m.p. 142–143° (EtOH), overall yield 80%. IR: no band in the CO region. NMRδ H_2, H_3 and H_4 at 5.26 broad s, 3.76 bd and 4.27 d respectively ($J_{2,3} = 0.5$ and $J_{3,4} = 4.8$ Hz); OCH_2 at 3.16 dq, 3.45 dq, 3.61 dq and 4.08 dq, CH_3 at 0.88 t and 1.26 t. (Found: C, 72.57; H, 6.58; N, 7.82. Calc for $C_{22}H_{24}N_2O_3$: C, 72.50; H, 6.64; N, 7.69%).

From the first fraction eluted a 20% yield of **4d** was obtained as an oil. IR: no band in the CO region. NMRδ H_2, H_3 and H_4 at 5.41 d, 3.60 dd and 4.16 d respectively ($J_{2,3} = 2.4$ and $J_{3,4} = 9.9$ Hz); OCH_2 at 3.15 dq, 3.41 dq, 3.80 dq and 3.94 dq, CH_3 at 0.94 t and 1.24 t. (Found: C, 73.03; H, 6.32; N, 7.33. Calc for $C_{22}H_{24}N_2O_3$: C, 72.50; H, 6.64; N, 7.69%).

Reaction of 1 *with* **2e**. A mixture of 1 (2 mmoles) and **2e** (10 mmoles) was heated at 105° for 1 hr into a sealed glass tube previously washed with a soln of 5% NaOHaq and subsequently dried. The viscous orange oil was chromatographed (Silicagel G Merck, cyclohexane/EtOAc 90:10 as eluant) and the light amber oil spontaneously solidified into a white solid. When crystallized from EtOH/H_2O colourless crystals of **3e** were obtained; m.p. 65–66° (nearly quantitative yield). IR: no band in the CO region. NMRδ H_4 at 4.38 s, $(OCH_2)_4$ at 3.4–4.1 m, CH_3 at 1.04 t, 1.11 t, 1.14 (6H) t. (Found: C, 68.78; H, 7.19; N, 6.18. Calc for $C_{26}H_{32}N_2O_5$. C, 69.00; H, 7.13; N, 6.19%).

Kinetic determinations

The xylene solvent used for the kinetic runs was redistilled reagent grade (mixture of isomers). The overall reaction rates were measured by following the disappearance of 1 at 328 nm on a Beckman DU-2 spectrophotometer, solutions were measured in 1.00 cm OS Hellma cells of 3 ml capacity. Two general methods were followed.

Method A (*used for* **2b**). A sample of 1 (in the range 0.0007–0.0015 M) was accurately weighed into a 10 ml volumetric flask and dissolved in xylene. A sample of **2b** (0.1–0.5 M) was accurately weighed into a thin sealed glass tube, added into a 10 ml volumetric flask and broken under xylene. A portion (0.05 or 0.1 ml) of the soln of 1 was removed with a microsyringe and added to the cell previously filled with 3.00 ml of xylene. The cell was housed in the spectrophotometer cells compartment previously thermostatted at the required temp. A portion of the soln of **2b** (0.1, 0.2 or 0.3 ml in order to ensure a wide range of concentrations) was removed with the microsyringe and added to the cell shaking the resulting soln. At appropriate time intervals (0.5–5 min) the absorbance was determined and the reaction followed to 60–80% completion. The results fit the first-order equation and hence pseudo-first-order rate constants were determined.

Some preliminary experiments at 63.5° with lower concentrations of **2b** gave results fitting the second-order rate equation with both rate constants in good agreement (Table 4) therefore showing the reaction to be a second-order, first-order with respect to each reagent. The kinetic data are the average of 7–9 kinetic runs the extreme values being excluded.

Table 4. Rate constants for the reaction of 1 (initial concn. C_P) and **2b** (initial concn. C_E) at 63.5° in xylene

Run	$10^4 C_P$	$10^4 C_E$	C_E/C_P	$10^1 \times k$
1	0.36	3.44	9.56	1.93[a]
2	0.31	7.33	23.65	2.07[a]
3	0.39	56.60	145.13	2.17[b,c]
4	0.33	70.19	212.70	2.28[b]
5	0.33	79.17	239.91	2.38[b]
6	0.38	109.78	288.89	2.30[b]
7	0.32	136.12	425.38	2.64[b]
8	0.18	81.73	454.06	2.70[b,c]
9	0.32	153.55	479.84	2.45[b]

a) Second-order rate constants (l mol^{-1}s^{-1}).

b) Pseudo-first-order rate constants (l mol^{-1}s^{-1}).

c) Extremes values excluded.

Method B (used for **2a**, **2c–e**). A sample of **1** (in the range 0.0005–0.0015 M) was accurately weighed into a 50 ml volumetric flask (10 ml for **2d**) and dissolved in xylene. A sample of ethoxyethene (in the range 0.10–0.70 M) was accurately weighed into a thin sealed glass tube, the reagents were mixed and xylene added up to the required volume. Immediately 0.20 ml portions of the homogeneous solution were removed with a microsyringe and placed in sealed glass tubes. About 10–12 samples were prepared for each run. At time zero the samples were placed into a water ultrathermostat at the required temp. and a 0.20 ml portion of the starting soln was diluted to 6.20 ml with xylene and the absorbance determined. At appropriate time intervals (from 5 min for **2a** at 95.2° to 500 min for **2d** at 63.5°) the residual absorbance at 328 nm was measured after dilution to 6.20 ml with xylene. The kinetic data reported in Table 1 are the average of three to five kinetic runs using different initial concentrations of pyrazolone and ethoxyethene for each run. Under the experienced conditions, pseudo-first-order rate constants were determined.

As a final suggestion, care must be taken to prepare the glass vials for the reactions involving **2e**. The inner surface of each vial must be washed with 5% NaOHaq and dried to avoid moisture, otherwise the eventual acidity of the glass gives irreproducible results.

CNDO/2 calculations MO calculations to the CNDO/2[19] level of approximation were performed on a 6040 Honeywell computer by using a QCPE 141 Program. The C_{2h} conformation was adopted for tetramethoxyethene and the C–C bond length and C–O–C angle (1.42 Å and 127° respectively) were chosen to minimize E_B (the total binding energy). All calculations for lower and higher values, which gave higher E_B, and all MOs parameters are available on request.

Table 5. Typical run for reaction of pyrazolone **1** (0.000032 M) with **2b** (0.015355 M) in xylene at 63.5°

Time (seconds)	A	Reaction %	10^{1}xK
0	0.694	--	--
20	0.641	7.64	2.60
40	0.597	13.98	2.46
60	0.551	20.61	2.49
80	0.513	26.08	2.47
100	0.476	31.41	2.46
120	0.442	36.31	2.45
150	0.393	43.37	2.46
180	0.354	48.99	2.45
210	0.315	54.61	2.45
240	0.284	59.08	2.44
270	0.252	63.69	2.44
300	0.224	67.72	2.44
330	0.200	71.18	2.45

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