Kinetics of the Decomposition of Some Δ^1-Pyrazolines

By **Donald E. McGreer,* Ian M. E. Masters,** and **Michael T. H. Liu,** Department of Chemistry, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1W5

Thermal decomposition of a series of 4- and 5-alkyl-substituted 3-methyl-3-methoxycarbonyl (or 3-acetyl)-Δ^1-pyrazolines has been investigated. The relative rates for the decomposition of these compounds were given. Two mechanisms are proposed, one for the formation of olefin and the other for the formation of cyclopropane, to account for the observed kinetic results and product distribution.

THE mechanism of the pyrolysis of Δ^1-pyrazolines has been under debate for many years and has been reviewed.[1,2] This research was conducted mainly on various substituted 3-methyl-3-methoxycarbonyl (or 3-acetyl)-Δ^1-pyrazolines and it was hoped that the kinetic results for these pyrazolines could be used in a mechanistic description of the decomposition reaction.

EXPERIMENTAL

Preparation of Δ^1-Pyrazolines.—The Δ^1-pyrazolines prepared for the present investigation are listed in Table 1. All compounds were prepared by the addition of a diazoalkane to the appropriate activated olefin. The Δ^1-pyrazolines thus prepared had spectral data in agreement with those reported in the literature. The n.m.r. spectrum of 3-acetyl-3,5,5-trimethyl-Δ^1-pyrazoline (8) shows an acetyl methyl signal at τ 7.68 and the non-equivalent C-5 methyl resonances at τ 8.58 and 8.76. The two hydrogens on C-4 show an AB signal with a pair of doublets at τ 7.90 and 8.92 (J_{gem} 13.4 Hz).

Products.—With the exception of 3-acetyl-3,5,5-trimethyl-Δ^1-pyrazoline (8), the identification and percentage composition of the thermal decomposition products of 1-pyrazolines

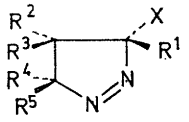
[1] C. H. Bamford and C. F. H. Tipper, 'Comprehensive Chemical Kinetics,' Elsevier, London, 1972, vol. 5, p. 585.

[2] R. G. Bergman, in 'Free Radicals,' ed. J. Kochi, Wiley–Interscience, New York, 1973, vol. 1, p. 191.

used in this work has been discussed.[3-10] We shall report the decomposition products of compound (8) only. Pyrolysis of 3-acetyl-3,5,5-trimethyl-Δ^1-pyrazoline (8) gave a mixture of six products, four of which were characterized by comparing them with authentic samples. The effect of solvents on the product distribution from this pyrazoline is given in Table 2.

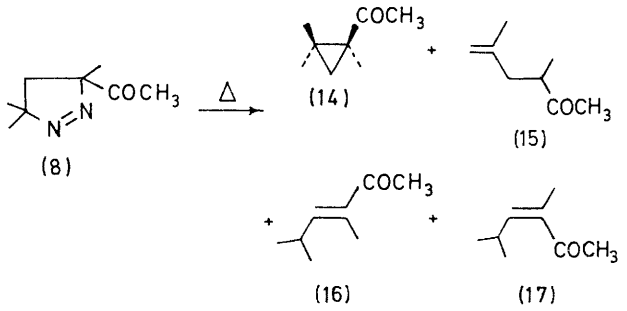
TABLE 1

Preparation of Δ^1-pyrazolines



Δ^1-Pyrazoline	X	R^1	R^2	R^3	R^4	R^5	Ref.
(1)	CO_2CH_3	CH_3	H	H	H	H	*a*
(2)	CO_2CH_3	CH_3	H	H	H	CH_3	3
(3)	CO_2CH_3	CH_3	H	H	CH_3	H	3
(4)	CO_2CH_3	CH_3	H	H	CH_3	CH_3	*b*
(5)	$COCH_3$	CH_3	H	H	H	H	4
(6)	$COCH_3$	CH_3	H	H	H	CH_3	4
(7)	$COCH_3$	CH_3	H	H	CH_3	H	4
(8)	$COCH_3$	CH_3	H	H	CH_3	CH_3	This work
(9)	CN	CH_3	H	H	H	H	*c*
(10)	CO_2CH_3	CH_3	H	CH_3	H	H	5
(11)	CO_2CH_3	CH_3	CH_3	H	H	H	5
(12)	CO_2CH_3	CH_3	H	CH_2CH_3	H	H	6
(13)	CO_2CH_3	CH_3	CH_2CH_3	H	H	H	6

[a] H. R. Snyder, Ph.D. Thesis, Boston University, 1958. [b] N. W. K. Chiu, Ph.D. Thesis, University of British Columbia, 1967. [c] D. Gotkis and J. B. Cloke, *J. Amer. Chem. Soc.*, 1934, **56**, 2710.



Kinetic Procedure.—The rates of decomposition of pyrazolines studied were determined by the nitrogen evolution method. The bath temperature was controlled to $\pm 0.05°$. The first-order rate coefficients were determined graphically from the plot of log $[V_\infty/(V_\infty - V_t)]$ against time where V_∞ is the volume of nitrogen measured at infinite time (10 half-lives) and V_t is that at time t. The detail description of these measurements were given in our earlier work.[11]

RESULTS AND DISCUSSION

The results of the kinetic studies are summarized in Table 3. To facilitate a comparison with a standard pyrazoline (1), relative rates for a number of C-3 and C-5 substituted pyrazolines are given in Table 4. The numbers given here represent relative rates k(pyrazolines)/k(1) at 109.4° in n-butyl phthalate solvent.

TABLE 2

Product compositions for the pyrolysis of 3-acetyl-3,5,5-trimethyl-Δ^1-pyrazoline (8)

Reaction conditions	Δ (14)	γ,δ* (15)	α,β *cis* (16)	α,β *trans* (17)	Total of unknown products
Neat at 109°	68	9	9	14	Trace
100° in n-butyl phthalate	66.5	9.5	9.5	9.8	4.7
100° in formamide	17.6	6.8	5.7	66.0	3.9

* (15) is the thermal rearrangement product of (14); not a direct product from the pyrazoline decomposition (R. M. Roberts, R. G. Landolt, R. N. Greene, and E. W. Heyer, *J. Amer. Chem. Soc.*, 1967, **89**, 1404).

TABLE 3

Summary of the rate constants in the pyrolysis of Δ^1-pyrazolines in n-butyl phthalate

Compound	T/°C	10^4k/s^{-1}
	107.3	0.662
(1)	116.1	1.75
	127.0	5.63 ± 20 [a]
	109.4	6.77
(2)	99.7	2.63
	89.75	0.857
	109.4	8.48
(3)	99.7	3.17
	89.75	1.03
(4)	109.4	4.26 ± 0.10
	127.0	9.61
(5)	117.0	3.46
	106.8	1.18
(6)	109.4	13.6
	109.4	17.0
(7)	99.7	6.47
	89.8	2.22
(8)	109.4	8.89 ± 0.20
	89.9	1.09
	109.4	7.34 ± 0.20
(9)	9.7	2.58
	89.25	0.765
	147.4	13.1
(10)	137.1	4.60
	127.1	1.61
	157.2	5.11
(11)	147.4	1.59
	137.0	0.533
	147.4	5.64
(12)	137.2	1.81
	127.0	0.529
(13)	157.2	2.91
	147.4	1.03

[a] Error limits are expressed as either the standard deviation or the average deviation from the mean.

Increasing electron-withdrawing ability at C-3 enhances the rate of decomposition as shown in going from compounds (1) to (5) to (9) in Table 4. This would suggest that a small charge was developing at C-3 in the

[3] D. E. McGreer, N. W. K. Chiu, M. G. Vinje, and K. C. K. Wong, *Canad. J. Chem.*, 1965, **43**, 1407.
[4] D. E. McGreer, N. W. K. Chiu, and M. G. Vinje, *Canad. J. Chem.*, 1965, **43**, 1398.
[5] T. V. van Auken and K. L. Rinehart, jun., *J. Amer. Chem. Soc.*, 1962, **84**, 3736.
[6] D. E. McGreer and W. S. Wu, *Canad. J. Chem.*, 1967, **45**, 461.
[7] D. E. McGreer, *J. Org. Chem.*, 1960, **25**, 852.
[8] D. E. McGreer, W. Wai, and G. Carmichael, *Canad. J. Chem.*, 1960, **38**, 2410.
[9] D. E. McGreer, P. Morris, and G. Carmichael, *Canad. J. Chem.*, 1963, **41**, 726.
[10] D. E. McGreer, R. S. McDaniel, and M. G. Vinje, *Canad. J. Chem.*, 1965, **43**, 1389.
[11] D. E. McGreer and I. M. E. Masters, *Canad. J. Chem.*, 1969, **47**, 3975.

transition state. The effect of a methyl substituent at C-5 generally increases the rates of decomposition of 3-methoxycarbonyl- and 3-acetoxy-Δ^1-pyrazoline. This trend was brought out by the fact that the activation enthalpies were lowered for all the C-5 substituted compounds as compared with the unsubstituted ones. The relative rates in Table 4 were also in agreement with the foregoing statement. The enhancement in rate indicates that the C(5)–N bond is slightly weakened by methyl substitution at C-5. The two-fold rate increase upon substitution of the methoxycarbonyl by an acetyl

TABLE 4

Effect of 5-methyl substitution on the rates of decomposition of 3-methoxycarbonyl- and 3-acetyl-Δ^1-pyrazolines in n-butyl phthalate at 109.4°.

Compound	Rel. rate
(1)	1.00
(2)	8.16
(3)	10.2
(4)	5.13
(5)	1.87
(6)	16.4
(7)	20.2
(8)	10.7
(9)	8.85

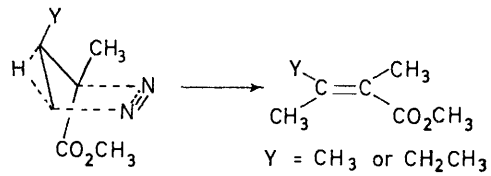
TABLE 5

Effect of 4-alkyl substitution on the rate of decomposition of 3-methoxycarbonyl-Δ^1-pyrazolines in n-butyl phthalate at 147.4°

Compound	Rel. rate
(1)	1.00
(10)	0.31
(11)	0.037
(12)	0.13
(13)	0.024

group is maintained even with substitution of methyl(s) at C-5; for example, consider (2) compared with (6), (4) compared with (8). This suggests that there is very little electronic C(3)–C(5) interaction in the transition state for pyrazoline pyrolysis. However, the stereochemistry of the 5-methyl group has very little effect on the pyrolysis rates, the *trans*-isomers (3) and (7) decomposing only slightly faster than the *cis* (2) and (6).

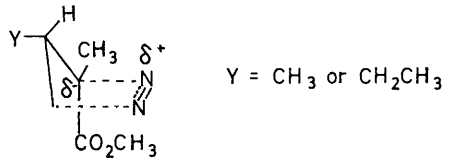
Table 5 shows that 4-alkyl substitution decreases the rate of pyrolysis compared with (1), as exemplified by the increase in activation enthalpies for all the 4-alkyl substituted compounds. This decrease in rate depends not only on the size of the alkyl group but also on the stereochemistry of the substituents on the ring. The *cis*-isomers (10) and (12) decompose faster than the *trans* (11) and (13); the rate of pyrolysis of (12) is 2.3 times slower than of (10) indicating that the bulkiness of the C-4 ethyl group in (12) has an overall effect on rate. In the pyrolysis of *cis*- and *trans*-3,5-dimethyl-3-methoxycarbonyl-Δ^1-pyrazoline, the *cis*-pyrazoline gives *cis*-$\alpha\beta$-unsaturated olefin while the *trans*-pyrazoline gives *trans*-$\alpha\beta$-unsaturated olefin.[3] This, together with McGreer and Masters' studies on pyrolysis of deuteriated pyrazolines,[11] suggests that the transition state for the formation of olefin must favour structure (18) wherein the C-4 hydrogen *trans* to the leaving nitrogen migrates to C-5. This feature is the primary indication that a mechanism compatible to that proposed by Crawford [12] for alkyl-substituted pyrazolines is not applicable in the present cases, as we have elaborated elsewhere.[6]



(18)

Bulky groups at C-4 are expected to adopt a pseudo-equatorial position and thus the observation that *cis*- and *trans*-4-t-butyl-3-methyl-3-methoxycarbonyl-Δ^1-pyrazoline yields only a single cyclopropane product in each case further supports the requirements of structure (18).[13]

In view of the observed solvent effects and also of the substituent effects, we have reason to believe that the transition state leading to the formation of cyclopropane derivatives is of polar character as given in (19). This



(19)

structure has a polarized C-3–N bond and the extent of polarization would depend on the substituent present in the pyrazoline ring.

We also believe that the decomposition is concerted but the degree of bond breaking of the C-3–N bond is well advanced over the bond breaking of the C-5–N bond. Although (19) is suggested to be the transition state for the formation of cyclopropane, it is to be noted that this pathway is not favoured by an increase of solvent polarity. Table 2 shows that in the pyrolysis of 3-acetyl-3,5,5-trimethyl-Δ^1-pyrazoline (8), the formation of cyclopropane was reduced from 66.5 to 17.6% in going from n-butyl phthalate to formamide. A similar trend was observed in the pyrolysis of 3-methyl-3-methoxycarbonyl-Δ^1-pyrazoline (1).[11] In this pyrolysis also a small decrease in rate constants was observed in going from tetralin to n-butyl phthalate to nitrobenzene and finally to formamide.[11]

These data appear to suggest that the polarizability of the carbonyl group (in $COCH_3$ or CO_2CH_3) decreases in polar solvents because of dipole–dipole interactions with the solvent and hence, its ability to stabilize (19) is

[12] (*a*) R. J. Crawford and A. Mishra, *J. Amer. Chem. Soc.*, 1966, **88**, 3963; (*b*) A. Mishra and R. J. Crawford, *Canad. J. Chem.*, 1969, **47**, 1515.

[13] S. Szilagyi, Ph.D. Thesis, University of British Columbia, 1974.

reduced. Dipole–dipole interactions of the C=O group with formamide is also indicated by the relative amounts of αβ unsaturated olefin formed from (8) (Table 2). The predominance of the *trans*-product over the *cis* (66 : 5.7) suggests that the O=C–CH_3 group has a much greater steric requirement due to solvent interactions favouring migration of one of the C-4 hydrogens over the other.

In the pyrolysis of 3-cyano-3-methoxycarbonyl-Δ^1-pyrazoline, it was observed that the rate increases with increase in solvent polarity.[14] It is clear from this example that two electron-withdrawing groups are more effective in stabilizing a negative charge at the 3-position and their effect is not compensated by other solvent interactions.

To sum up, two transition states are proposed in the pyrolysis of the Δ^1-pyrazoline (1), one for the formation of olefin and the other for the formation of cyclopropane. The enthalpies of activation for pyrolysis of *cis*- and *trans*-4-t-butyl-3-methyl-3-methoxycarbonyl-Δ^1-pyrazoline (in n-butyl phthalate) are 149.3 and 151.5 kJ mol^{-1} respectively although only cyclopropanes are formed. Similarly substituted pyrazolines (10)—(13) which give mixtures of olefin and cyclopropanes have enthalpies of activation of 141.4, 161.9, 159.4, and 157.3 kJ mol^{-1}. The enthalpy of activation for olefin formation is therefore similar to that for cyclopropane formation.

[5/785 *Received*, 28*th April*, 1975]

[14] D. E. McGreer and Y. Y. Wigfield, *Canad. J. Chem.*, 1969, **47**, 3965.