Tetrahedron Letters,Vol.27,No.14,pp 1575-1576,1986 0040-4039/86 $3.00 + .00
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MECHANISM OF THE (O---H---O) HYDROGEN TRANSFER IN ENE REACTIONS

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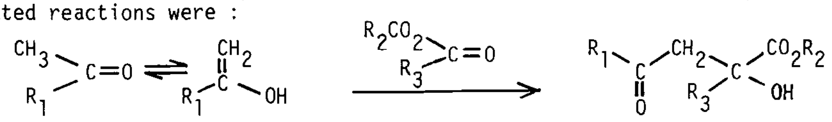
The ene reaction between a ketone and an activated carbonyl bond proceeds in a concerted pathway on the basis of the volume of activation determined from high pressure kinetics.

The ene reaction, closely related to the [4+2] cycloaddition, was discovered a long time ago by Alder[1]. The reaction found, however, only few synthetic applications until recently. The renewed interest is due to the use of new enophiles allowing milder temperature conditions[2]. High pressures were also used as a synthesis tool to generate new compounds via ene reactions[3].

This methodology provides in addition a means to locate the transition state along the reaction coordinate via the volume of activation given by a study of the pressure dependence of the reaction rate[4]. Among the numerous addition reactions investigated by this procedure, ene reactions were also considered[5]. The allylic hydrogen abstraction by an activated carbonyl bond from linear olefins, depicted as (C---H---O) hydrogen transfer was found to occur according to a concerted process in which the hydrogen atom is abstracted in a non-linear fashion. The main argument was that the absolute value of the volume of activation $\Delta V^{\neq}$ was invariably found as greater than the reaction volume (meaning that the transition state is more "compressed" than the products)[5].

However, the prevailing of the concertedness for other hydrogen transfer reactions may be questioned. This interrogation prompted us to consider the ene reaction between keto compounds and activated carbonyl bonds, termed here as (O---H---O) hydrogen transfer. The investigated reactions were :



$R_1 = CH_3$, $R_2 = C_2H_5$, $R_3 = C_2H_5CO_2$ (reaction A)
$R_1 = C_2H_5CO_2CH_2$, $R_2 = CH_3$, $R_3 = C_6H_5$ (reaction B).

These reactions were shown as occuring with great ease[6] at temperatures of 120°C. They proceed via the enol form and the keto compound. We have examined the solvent effect (Table 1) and the pressure effect (Table 2) on the kinetics.

Table 1

Solvent dependance of rate constant k (a)

	Reaction	cyclohexane	toluene	benzene	choloroform	acetonitrile	acetone
10^2k (h^{-1})	A	-	1.22	-	0.91	-	3.64
10^3k ($l.m^{-1}.h^{-1}$)	B	2.84	-	2.56	3.06	3.85	-

(a) T_A (97.0°C), T_B (100.8°C). Rates were determined by GC (FFAP, 100-240°C, 6°C/min.).

The polarity of the solvent affects the reaction rate only to a small extent. Such result precludes the existence of a zwitterionic intermediate in accordance with the results previously found for the (C---H---O) transfer[7]. To relieve the dichotomy between the diradical mechanism and the concerted pathway, we have investigated the pressure effect upon the reaction rate. However, reaction B gave scattered kinetic results under pressure which are not reported in Table 2.

Table 2

Pressure effect on rate constant k in reaction A (a)

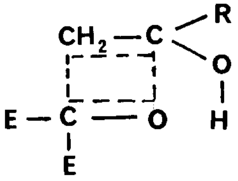
Pressure (bar)	10^2k (h^{-1})	
0.1	3.64	
260	4.91	$\Delta V^{\neq}_{20}$ = -30.0 + 1.0 cm^3/mole (b)
485	6.22	
720	8.61	ΔV_{20} = -33.9 + 0.1 cm^3/mole (b)
1420	17.9	

(a) The first-order rate constants calculated from GC data were not corrected in function of pressure[8]. Acetone served as solvent and T was 97.0°C.

(b) The $\Delta V^{\neq}$-value determined at the reaction temperature T was calculated for T = 20°C according to Elyanov's formula[5]. The reaction volume ΔV was determined as the difference of the molar volumes of product and reactants.

The values of $\Delta V^{\neq}$ and of the ratio $\Delta V^{\neq}$: ΔV suggest a product-like transition state[4]. In other words, breaking of the first O-H bond and formation of the second H-O bond should occur about the same time. Whether the rate-determining H-transfer step takes place in an angular fashion or according to a linear process cannot be deduced unequivocally from the data. In the present study, $\Delta V^{\neq}$ is smaller than ΔV, thus differs from the values found in the earlier study relative to the (C---H---O) transfer[5].

Kwart suggested for the (C---H---O) transfer a [2+2] cyclic complex lying close to the transition state[9], like in the present case :



The rigidity of such intermediate should be supported by high negative values for $\Delta V^{\neq}$. While this view is quite conceivable for the (C---H---O) transfer, a [2+2] preformed complex in the present reactions is unlikely, because the reaction partners are electronically similar and the volume of activation does not exhibit an anomalous value.

We rather conclude that the (O---H---O) transfer in the present ene reactions proceeds in a concerted pathway with a "late" product-like transition state. High pressure kinetics of other hydrogen transfer reactions are under investigation.

REFERENCES

1) K. Alder, J. Pascher and A. Schmitz, Chem. Ber., 76, 27 (1943).
2) N. Schönberger and G. Kresze, Liebigs Ann. Chem., 1725 (1975) ; G. Deleris, J. Kowalski, G. Dunogues and R. Calas, Tetrahedron Lett., 4211 (1977) ; G. Gill and K.S. Kirollos, Tetrahedron Lett., 23, 1399 (1982) ; O. de Lucchi, L. Pasquato and G. Madera, Tetrahedron Lett., 25, 3647 (1984).
3) J.A. Gladysz and Y.S. Yu, J. Chem. Soc., Chem. Comm., 599 (1978).
4) G. Jenner, Bull. Soc. Chim. France, II-275 (1984).
5) G. Jenner and M. Papadopoulos, J. Org. Chem., 47, 4201 (1982).
6) O. Achmatowicz and M.Pietraszkiewicz, Tetrahedron Lett., 22, 4323 (1981).
7) O. Achmatowicz and J. Szymoniak, J. Org. Chem., 45, 1228 (1980).
8) S.D. Hamman and W.J. le Noble, J. Chem. Educ., 61, 658 (1984).
9) H. Kwart and M.W. Brechbiehl, J. Org. Chem., 47, 3353 (1982).

(Received in France 10 February 1986)