

OXIDATION OF α -AMINO ACIDS BY PERMANGANATE: ISOKINETIC RELATION

Maria J. INSAUSTI, Maria P. ALVAREZ-MACHO and Fernando MATA-PEREZ

*Departamento de Química Física,**Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain*

Received November 14, 1991

Accepted February 12, 1992

The oxidation of three α -amino acids by permanganate under neutral conditions has been studied at various temperatures. The use of Exner's statistical method shows no existence of an isokinetic relation in the heterogeneous process but for the homogeneous process such a relation has been found. Moreover, the existence of linear free energy relations was confirmed for the homogeneous process.

Mechanistic information obtained from temperature effect on the experimental rate constant is normally discussed in terms of enthalpy and entropy of activation. This information can be obtained by means of the empirical Arrhenius equation (1)

$$k = A \exp(-E_a/RT) \quad (1)$$

or by the thermodynamic version of Eyring's equation (2)

$$k = kT/h \exp(\Delta S^\ddagger/R) \exp(-\Delta H^\ddagger/RT) \quad (2)$$

From the activation parameters the isokinetic relation (IKR) or compensation law¹ can be obtained:

$$\Delta H^\ddagger = \Delta H_0^\ddagger + \beta \Delta S^\ddagger \quad (3)$$

where β , called isokinetic temperature (T_{iso}), represents the temperature at which all the reactions would proceed at the same reaction rate. From this relation information about the electronic effect of the substituents, solvent effect, etc. can be obtained.

There are several papers^{2,3} which demonstrate that obtaining T_{iso} by the Eq. (3) can lead to erroneous results, due to the interdependence which exists between ΔH^\ddagger and ΔS^\ddagger , their errors also being directly related. This could explain why the linear relation between activation parameters is in some cases only a correlation of experimental errors and not the isokinetic relation.

Exner^{4,5} and Exner and Beránek⁶ have developed a statistical method for calculation of the value of T_{iso} based on Arrhenius equation. The traditional method was improved by experimental tests⁷⁻¹⁰. The correlation of $\ln k$ with $1/T$ yields a series of straight lines which should intersect at a point in which the abscissa is precisely $1/T_{iso}$, when its value is calculated by the least squares method. One condition must be fulfilled for this isokinetic relation being acceptable: the standard deviation s_0 of the restricted linear regression is not much greater than the standard deviation s_{00} of the linear regression without restriction. When the values for s_{00} and s_0 are similar, it is necessary to calculate the distribution function, \bar{F} ; only when the value of \bar{F} is less than one, an isokinetic relation exists. On the other hand, it can be stated that the existence of an IKR is essential for free energy relations (LFER) to exist, such as correlations of the type of Brønsted, Hammet, Taft, Reichardt, etc.

The object of this study has been to study the possible existence of an IKR among the activation parameters of the permanganic oxidation of α -amino acids (glycine, alanine and phenylalanine) and to verify the fulfillment of Taft equation.

EXPERIMENTAL

Materials. The Merck p. a. quality reagents were used: potassium permanganate, glycine, phenylalanine, alanine, potassium hydrogen phosphate and potassium dihydrogen phosphate. The mixture of KH_2PO_4 - K_2HPO_4 was used with the purpose of maintaining pH of the medium constant and of stabilizing manganese dioxide (the product of the reaction) as a soluble colloid throughout the reaction¹¹. The solvent used was distilled water.

Kinetic measurements. The kinetic measurements were carried out with a Spectronic 1201 spectrophotometer, which enables to follow the reactions at various wavelengths; the instrument was provided with an internal thermostated system connected to a Selecta thermostat, Frigiter model, which ensured constant temperature within ± 0.05 °C. The course of the reaction has been followed by measuring the disappearance of Mn(VII) at 525 nm and the appearance of Mn(IV) at 418 nm. In all of the experiments potassium permanganate was used at $5 \cdot 10^{-4}$ mol l⁻¹ concentration, i.e. much lower than that of the α -amino acids (0.05 mol l⁻¹).

pH of the solution was always 7.0 (a Radiometer model 51 pH-meter with a combined glass-calomel electrode was used for its control). The buffer concentration necessary for maintaining this pH value constant resulted in an ionic strength of 0.66 mol l⁻¹.

The oxidations of glycine, phenylalanine and alanine by permanganate are of an autocatalytic type¹²⁻¹⁴, the Mn(IV) formed in the reaction being responsible for the autocatalysis. These reactions thus take place by two different routes, as a non-catalyzed homogeneous process and as a catalyzed heterogeneous process. Therefore, the rate equation can be written in the following form:

$$-dc/dt = k_1 c + k_2 c (c_0 - c), \quad (4)$$

where c represents the reagent concentration, c_0 is the initial concentration, and $(c_0 - c)$ is the concentration of the product, while k_1 and k_2 are the pseudo-rate constants corresponding to the homogeneous and heterogeneous processes, respectively. The values of k_1 and k_2 can be obtained from the integrated rate equation by an iterative method¹⁴ (Eq. (5)).

$$\ln (k_1 + k_2 c_0 - k_2 c) / c = \ln (k_1 / c_0) + (k_1 + k_2 c_0) t \quad (5)$$

RESULTS AND DISCUSSION

The study of the effect of temperature on the rate constants of oxidation of glycine, phenylalanine and alanine by permanganate was made in the region of 28 to 46 °C. The values obtained for k_1 and k_2 are shown in Table I, the activation parameters being presented in the same table.

TABLE I

Effect of temperature on the homogeneous and heterogeneous process of permanganate oxidation (for conditions see Experimental; k_1 and k_2 in $l\ mol^{-1}\ s^{-1}$); G glycine, A alanine, PA phenylalanine

Temperature °C	G		A		PA	
	$k_1 \cdot 10^3$	k_2	$k_1 \cdot 10^3$	k_2	$k_1 \cdot 10^3$	k_2
28	0.858	0.548	1.210	0.085	1.060	0.796
31	0.987	0.735	1.500	0.119	1.230	1.020
34	1.100	0.971	1.850	0.171	1.490	1.350
37	1.270	1.280	2.600	0.223	1.840	1.720
40	1.490	1.730	3.060	0.316	2.240	2.220
43	1.630	2.170	3.770	0.429	2.710	2.940
ΔH^\ddagger , $kJ\ mol^{-1}$	31.9	70.8	59.1	82.5	48.0	66.1
ΔS^\ddagger , $J\ mol^{-1}\ K$	-198	-15	-105	9	-143	-28

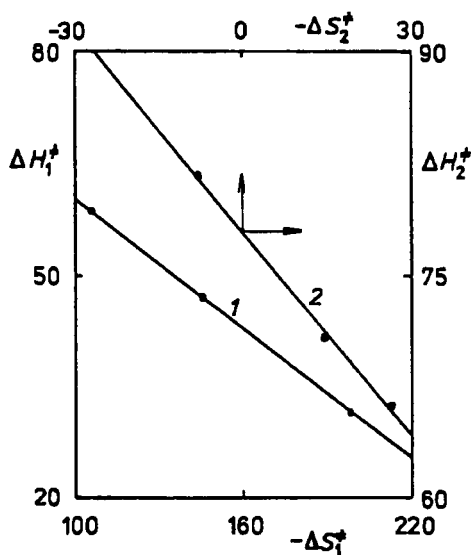


Fig. 1

Relation between activation parameters. For conditions see Experimental ($r_{xy} = 0.9999$ for homogeneous process (1) and $r_{xy} = 0.9953$ for heterogeneous process (2), ΔH^\ddagger in $kJ\ mol^{-1}$ and ΔS^\ddagger in $J\ mol\ K^{-1}$)

The representation of ΔH^* vs ΔS^* (statistically wrong) indicates a linear relation between the activation parameters in both cases (Fig. 1), but this finding is confirmed by a correct statistical only in one case.

The statistical method of Exner has been applied for these two methods by means of a Basic programme¹⁵; the results are presented in Table II. No isokinetic relation has been found for the heterogeneous reaction that $s_{00} = s_0$ and the distribution function is greater than unity ($\bar{F} = 1.62$). In contrast, for the homogeneous reaction as isokinetic relation (Fig. 2) guaranteed by the values of the standard deviations $s_{00} = s_0$ and by the

TABLE II
Statistical analysis of the homogeneous and heterogeneous process of permanganate oxidation

Quantity	Homogeneous reaction	Heterogeneous reaction
T_{iso} , K	290	-
$\ln k_{iso}$	-7.6439	-
s_{00} (no restriction)	0.0413	0.0749
s_0 (iso-kinetic)	0.0408	0.0811
s_{∞} (iso-enthalpic)	0.0905	0.0860
s_S (iso-entropic)	0.0947	0.0773
s_X (between reactions)	0.0393	0.0781
\bar{F} (distribution function)	0.334	1.623

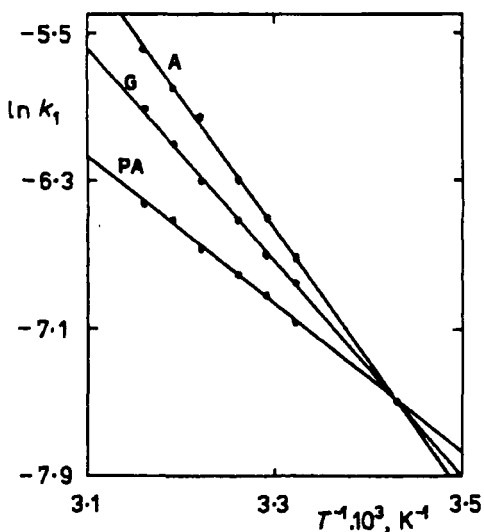


FIG. 2
Evidence for the existence of the isokinetic relation: homogeneous process. For conditions see Experimental (A alanine, $r_{xy} = 0.9983$; G glycine, $r_{xy} = 0.9992$; PA phenylalanine, $r_{xy} = 0.9973$)

distribution function $\bar{F} = 0.33$ was found. In addition, taking the value of $T_{iso} = 290$ K, in relation to the temperature interval, shows that it exists here a compensation effect¹⁶.

The existence of the IKR in a series of similar reactions indicates, as mentioned before, that lineal free energy relations LFER can be fulfilled^{16,17}. One relation of this type is the well known Taft equation:

$$(\forall T) \log k_{pT} = \log k_T^0 + \rho_T \sigma, \quad (6)$$

where k is the velocity constant, k^0 the constant for the model mixture, σ the polar constant of the substituent and ρ the reaction constant¹⁸. The plot of $\log k$ vs σ should give a straight line whose slope gives the reaction constant. Figure 3 shows a linear relation of this type for the homogeneous process, but not for the heterogeneous one. This is consistent with the existence of the IKR in only the first case. This fact allows us to conclude that the homogeneous mechanism of permanganate oxidation of the α -amino acids, at pH 7.0, takes place in a similar manner for the three species investigated (glycine, alanine and phenylalanine)^{19,20}. In contrast, the lack of the IKR, and consequently the non validity of Taft equation for the heterogeneous mechanism can be due to the specific effect that amino acids exert on the formation of the MnO_2 colloid autocatalyst. Indeed, in investigations currently in progress^{11,13}, we have demonstrated that although glycine and phenylalanine participate in the nuclear structure of the colloid reaction product, MnO_2 , the molecules of alanine do not participate, thus preventing the correlation among the three species to exist.

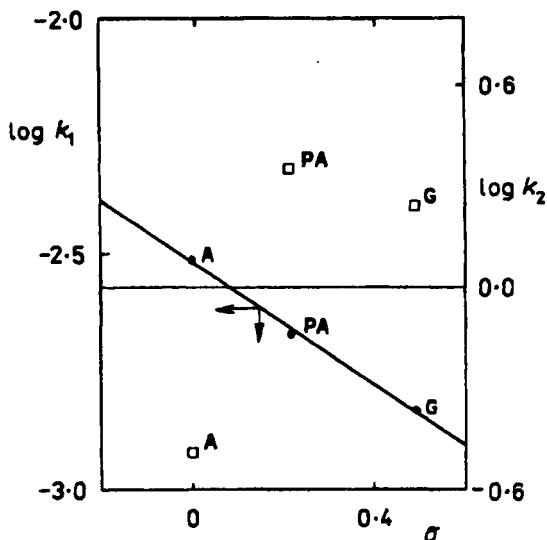


FIG. 3
Taft relationship for the homogeneous and heterogeneous process ($r_{xy} = 0.9932$ for the homogeneous process; for designation of compounds see Fig. 2). Squares denote heterogeneous process

REFERENCES

1. Exner O.: Collect. Czech. Chem. Commun. 29, 1094 (1964).
2. Petersen R. C.: J. Org. Chem. 29, 3133 (1964).
3. Exner O.: Collect. Czech. Chem. Commun. 40, 2762 (1975).
4. Exner O.: Collect. Czech. Chem. Commun. 37, 1425 (1972).
5. Exner O.: Phys. Org. Chem. 10, 411 (1973).
6. Exner O., Beránek V.: Collect. Czech. Chem. Commun. 38, 781 (1973).
7. Segura P.: Collect. Czech. Chem. Commun. 50, 1565 (1985).
8. Alvarez-Macho M. P., Montequi-Martin M. I.: Studia Chem. 13, 59 (1988).
9. Alvarez-Macho M. P., Montequi-Martin M. I.: Studia Chem. 14, 87 (1989).
10. Alvarez-Macho M. P., Mata-Perez F.: An. Quim. 85, 341 (1989).
11. Insausti M. J., Mata-Perez F., Alvarez-Macho M. P.: An. Quim. 87, 821 (1991).
12. Insausti M. J., Mata-Perez F., Alvarez-Macho M. P.: An. Quim. 87, 877 (1991).
13. Insausti M. J., Mata-Perez F., Alvarez-Macho M. P.: Int. J. Chem. Kinet. 23, 593 (1991).
14. Insausti M. J., Mata-Perez F., Alvarez-Macho M. P.: An. Quim. 86, 710 (1990).
15. Linert W., Soupup R., Schmid R.: Comput. Chem. 6, 47 (1982).
16. Exner O.: Prog. Phys. Org. Chem. 10, 2762 (1975).
17. Schmid R., Sapunov V. N.: *Non-Formal Kinetics in Search for Chemical Reaction Pathways*. Verlag Chemie, Weinheim 1982.
18. Shorter J.: *Correlation Analysis of Organic Chemistry*. Wiley, Chichester 1982.
19. Linert W., Jameson R. F.: Chem. Soc. Rev. 18, 477 (1989).
20. Conner W. C., Linert W.: Orient. J. Chem. 5, 204 (1989).