THE EFFECT OF SOLVENTS ON THE OXIDATION OF BUTYRALDEHYDE CATALYSED BY FERROCENE

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Oxidation of butyraldehyde to butyric acid catalysed by ferrocene in 10 solvents has been described by kinetic equations for autocatalysis. Rate constants of these equations were correlated with the properties of solvents. The oxidation rate was found to be independent of viscosity and fluidity of the reaction medium, electrophilicity expressed by E_T function and the donor ability of solvents. Only in nonpolar solvents the oxidation rate depended on $(n_D)_s^{-2}$. The rate of the title oxidation reaction was dependent on the polarity of reaction medium which was characterized by dipole moment and by functions of dielectric constants and increased with increasing solvent polarity. A similar dependence was also obtained with the use of solubility parameter and cohesion pressure of solvents. The rate of the oxidation increases with increasing solubility of oxygen in solvents. These dependences were used to discuss some steps of the mechanism of this oxidation.

Oxidation of aldehydes by oxygen has been studied by a number of authors both from theoretical and practical point of view[1,2]. It is generally accepted that the reaction can be described by a set of consecutive and parallel radical reactions (of which some form closed cycle) of autocatalytic type. However, some steps are not known in detail. The study of solvent effects on the course of the oxidation of aldehydes has not yet been reported, although *e.g.* the oxidation of butyraldehyde was examined in different solvents[3-5]. The results show that kinetics of the oxidation depends on the properties of solvents. For analogous oxidations of hydrocarbons the dependence of oxidation rate (initiation and propagation) on solvent polarity has been exemplified[6-10], similarly as in the case of radical oxidation polymerisation of olefins[11-13] and decomposition of peroxides[14]. The present knowledge of solvent effects on the course of chemical reactions[15-17] and the use of many known specific parameters of solvent which characterize its properties makes it possible to study the course of the above reaction in more detail.

In the previous work[18] we reported on the oxidation of butyraldehyde by air catalysed with ferrocene in a series of 12 solvents. The reaction was described by a kinetic equation with fractional reaction orders and the correlation of rate constants proved that they are dependent on the polarity of reaction medium. In the present work we utilized experimental results of our previous work, improved the kinetic description of the oxidation and examined the effect of solvents in more detail.

EXPERIMENTAL

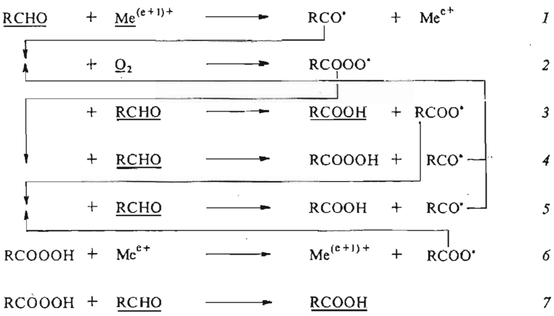
Oxidation of butyraldehyde was carried out in a flow, stirred reactor (50 ml of the reaction mixture) at 35°C into which oxygen (20 l/h) was introduced *via* a radial nozzle. The reaction mixture contained 50% of solvent (by volume) and 0·5 mol.% of ferrocene. Gas–liquid chromatographic analyses of butyraldehyde and butyric acid were used to construct conversion curves. For detailed description see a previous work[18].

Calculations of optimized values of rate constants were made with the own programme on Texas Instruments 59 calculator which was also used for regression analyses.

RESULTS AND DISCUSSION

On the basis of literature data[1–4,19,20] the overall reaction (*A*) can be depicted as follows (Scheme 1):

$$\mathrm{RCOH} + 1/2\,\mathrm{O_2} \xrightarrow{\mathrm{Me^{+e}}} \mathrm{RCOOH} \qquad (A)$$



SCHEME 1

Some studies[21,22] show that the reaction *2* is by nearly two orders of magnitude faster than reactions *3*, *4* or *1*, the sequence of which depends on the type of initiation. Oxidations catalysed by metal salts have propagation steps *3* or *4* as rate determining. Under the conditions used in this work the rate of reaction *7* is such that perbutyric acid concentration in the reaction mixture does not exceed 2 g/l.

Four-Parameter Approximation of Kinetic Description

In our previous work[18] the conversion curve for the oxidation of butyraldehyde was approximated by the kinetic equation for autocatalysis which involved the sequence of reaction steps *1*, *2*, *4* and *7*

$$\mathrm{d[BA]}/\mathrm{d}t = k_o[\mathrm{O_2}]^n\,[\mathrm{BAL}]^m\,([\mathrm{Me}]^{(e+1)+} + [\mathrm{R}])^p\,, \qquad (1)$$

where symbols in parentheses denote concentrations of compounds (BA – butyric acid, BAL – butyraldehyde) in mol/l, t is the reaction time in h, k_0 is the rate constant, $Me^{(c+1)+}$ can in the presence of oxygen and peroxo compounds be approximated by the analytical concentration of ferrocene, R is the concentration of autocatalytic products which – according to the reaction scheme – is proportional to the conversion of butyraldehyde into butyric acid. According to the work[23] the reaction order in oxygen is equal to 1 and the statistical analysis of standard deviations of average rate constants yielded the best values of the order $m = 1-1.5$ and $p = 0.5$ (the first one without statistical differentiation). To ensure consistency of treatment with the eight parameter approximation, also in this case we used the function Q for selection of the best equation. This function expresses the sum of weighed deviations of the independent variable-time, which is defined as follows[24],

$$Q_i = [(t_{i,\mathrm{calc.}} - t_{i,\mathrm{exp.}})\, r_i]^2 , \tag{2}$$

TABLE I

Chosen Orders in Kinetic Equations

For four parameter equations only four best equations are presented.

Eq.	Reaction order				H^a	S^b	α^c
	m	r	s	t			
	Four parameter equations						
(*1a*)	1	0·5	—	—	0·0755	14	—
(*1b*)	1·5	0·5	—	—	0·0867	17	69·5
(*1c*)	0·5	0·5	—	—	0·3477	25	99·9
(*1d*)	2	1	—	—	0·3920	26	99·9
	Eight parameter equations						
(*6a*)	1	—	1	0·5	0·0348	—	—
(*6b*)	1·5	—	1	0·5	0·0360	—	55·4
(*6c*)	1	—	0·5	1	0·0468	—	85·6
(*6d*)	1·5	—	0·5	1	0·0548	—	93·9

[a] Criterion of agreement according to Eq. (*3*); [b] standard deviation k; [c] the probability with which the studied equation can be excluded according to (*5*).

where $t_{i,\mathrm{exp.}}$ is the time necessary to attain the conversion of butyraldehyde in experimental point i, $t_{i,\mathrm{calc.}}$ is the time calculated in the same point with the use of average rate constant, r_i is the rate of change in butyraldehyde concentration (derivation of the conversion curve calculated analytically) in a given point i and n is the number of experimental points.

The final form of the decision function expressing the agreement between experimental and calculated curve in the concentration region given by experiment is defined as follows,

$$H = \sum_{i=1}^{n} (Q_i - Q_{i,\mathrm{max.}})/(n - 1) \qquad (3)$$

(it excludes the greatest deviation – the greatest error in the measurement).

Using this criterion, the best kinetic equation seems to be Eq. (*1a*) (Table I). Similarly as medium standard deviation of the rate constants also the difference in H values between Eq. (*1a*) and (*1b*) is not significant to the criterion of maximal likelihood. L_l/L_i is the criterion of maximal likehood of the compared set and the best set of data[24], N is the number of data for the set of solvents and α is the probability with which the compared equation can be excluded.

$$L_l/L_i = (H_i/H_l)^{N/2} \qquad (4)$$

$$\alpha = L_l/L_i : (L_l/L_i + 1) \qquad (5)$$

Eight Parameter Approximation of Kinetic Description

The eight parameter description of the kinetics of the reaction was used for two reasons. Increasing number of parameters in the kinetic equation leads to the better agreement between theoretical and experimental conversion curve, which is demonstrated in Fig. 1 on example of dimethylformamide as the solvent. Division of the expression for the rate of reaction (*6*) into two terms differentiates fictiously acyl radicals RCO$^\bullet$ formed by initiation reaction and those formed in the propagation step of the oxidation by chain transfer. The rate constant of the first term reflects also the effect of initiation reaction while the effect of initiation (step (*1*)) is not included in the second term.

$$\mathrm{d[BA]/d}t = k_0'[\mathrm{O_2}]^n\,[\mathrm{Me}^{(c+1)+}]^r\,[\mathrm{BAL}]^m + k_0''[\mathrm{O_2}]^u\,[\mathrm{BAL}]^s\,[\mathrm{R}]^t \qquad (6)$$

Provided that oxygen transport from the gas to liquid phase is sufficiently fast, the oxygen concentration can be considered as constant throughout the reaction and the constants can be defined as follows

$$k' = k'_0[O_2]^n \tag{7}$$

and

$$k'' = k''_0[O_2]^u\,. \tag{8}$$

Again, both constants will be a combination of the rate constants of elementary processes. On using $r = 1$ we started from the value reported by Lebedev[3,4] for the oxidation of butyraldehyde in methyl acetate. Orders m, s, t were chosen based on the experience with four-parameter approximation, in accordance with the best equations (*1a*) and (*1b*) (Table I). The other combinations of the orders m and $s = 1/2$; 1; 3/2; 2 and $t = 1/2$; 1; 2 yield greater deviations.

The solution of the eight parameter equation requires, however, an additional mathematical relation to Eq. (*6*). According to the type of condition of non-penetration, one can choose two approaches:

1) The additional equation can be obtained from the condition which defines the point of inflexion of autocatalytic curves, for which the first-order derivative of the rate of butyraldehyde consumption should equal to zero.

If constant C is defined as

$$C = k'[\mathrm{Me}^{(e+1)+}]/k'' \tag{9}$$

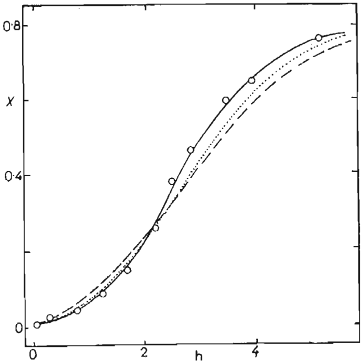


FIG. 1

Comparison of Experimental Conversion Curve for the Oxidation of Butyraldehyde in DMF (solid line) with Four Parameter Approximation (*1a*) (dashed line) and Eight Parameter Equation (*6a*) (dotted line) than from the condition of zero value of the derivative of conversion curve one obtains for C the following expressions in the case of Eqs (*6a*) and (*6b*) where A is the initial concentration of aldehydes and $X_{\max}$ is the concentration of aldehyde in the point of inflexion. Obtained C values were used to calculate k'' from integrated equations in the form for Eq. (*6a*) in which the variables are butyraldehyde concentration

$$C = 1/2(A - 3X_{\max})\,X_{\max}^{-0.5} \tag{10}$$

$$C = 1/3(A - 3X_{\max})\,(A - X_{\max})^{-0.5}\,X_{\max}^{-0.5} \tag{11}$$

$$\begin{aligned} k'_{6a}t = {} & 1/(\sqrt{A} - C)\ln\left[1 + \sqrt{(X/A)}\right] - 1/(\sqrt{A} + C)\ln\left[1 - \sqrt{(X/A)}\right] - \\ & - 2C/(A - C^2)\ln\left[1 + \sqrt{X/C}\right] \end{aligned} \tag{12}$$

and Eq. (*6b*).

$$\begin{aligned} k''_{6b}t = {} & C/\sqrt{[A(C^2 + 1)]}\left\{\ln\left|\frac{[\sqrt{(1 - X/A)} + 1/\sqrt{(C^2 + 1)}]\,[1 - 1/\sqrt{(C^2 + 1)}]}{[\sqrt{(1 - X/A)} - 1/\sqrt{(C^2 + 1)}]\,[1 + 1/\sqrt{(C^2 + 1)}]}\right| + \right. \\ & \left. + \ln\left|\frac{C/\sqrt{(C^2 + 1)} - \sqrt{(X/A)}}{C/\sqrt{(C^2 + 1)} + \sqrt{(X/A)}}\right|\right\} + 1/\sqrt{A}\ln\frac{1 + \sqrt{(X/A)}}{1 - \sqrt{(X/A)}} \end{aligned} \tag{13}$$

(X)-time (t) pairs. The constant C was determined from experimental data by graphical derivation of the conversion curve followed by determination of the position of maximum corresponding to the position of the point of inflexion on the original curve ($X_{\max}$). The inaccuracy of the graphical estimation of $X_{\max}$ causes an additional error in the calculation, even though this error is partly eliminated by graphical smoothing of the conversion curve, which increases the accuracy of the determination of butyraldehyde and butyric acid concentrations. This approach fails, however, in some cases, since experimental position of the point of inflexion does not fulfill mathemathical requirements for the calculation of constant C (see Eqs (*10*), (*11*) where C should be positive). The position of the inflexion in these cases is obviously complicated by further phenomena. For that reason these eight parameter equations were not used in the case of acetonitrile, butyraldehyde, acetic acid and toluene. Obtained values of k'' and k' were treated statistically as in the case of calculations according to equations of the type (*1*).

2) Another method for obtaining the additional condition of non-penetration is nonlinear regression in which we started from the condition of minimalisation of criterion H. Of variables k'' and C, the starting estimation of variable C was made on the basis of the values obtained by the above described method (where these values were available). By the method of one-dimensional network with variable density we determined k'' and C values which correspond to the minimal value of H in experimental points. For Eqs (*6c*) and (*6d*) and by using different inital C values we obtained several local minima, of which those further considered were minima with the lower H value. This method made it possible to use eight parameter equations also in those cases for which the graphical method has been unsuccessful.

Comparison of both methods is presented for curve (*6a*) in Table II. It is evident that in all cases the method of nonlinear regression yields the lower values of criterion H than the graphical method. For that reason only the values obtained by optimization method have been used in further treatment.

From Table I it is obvious that all the eight parameter equations tested fit experiment more closely than four parameter relations. According to the values of criterion H from Table I probably the best relation is Eq. (*6a*) where combination of the orders m, s and t corresponds to the best four parameter equation. Differences in the accuracy of fitting of experimental data between individual combinations of reaction orders are even smaller than in the case of the four parameter approximation due to the increased number of variable parameters.

TABLE II

Comparison of Graphical and Optimization Method for Calculation of Eight Parameter Equation (*6a*)

$(\sum_{i=1}^{N} H_i)/N$ graphical method 0·0311 optimization method 0·0172.

Solvent	Method[a]	k''_{6a}	k'_{6a}	C^b	H^c
n-Heptane	g	0·727	2·55	0·084	0·0304
	o	0·684	3·66	0·128	0·0274
Chlorobenzene	g	0·453	0·985	0·052	0·0202
	o	0·391	2·27	0·139	0·0075
Dioxane	g	0·380	4·56	0·287	0·0116
	o	0·346	1·89	0·131	0·0033
Isooctane	g	0·354	11·34	0·769	0·0165
	o	0·435	8·55	0·472	0·0135
Ethyl acetate	g	0·131	8·85	1·617	0·0231
	o	0·220	6·20	0·676	0·0028
Dimethylformamide	g	0·117	3·10	0·637	0·0847
	o	0·211	0·15	0·017	0·0485

[a] g Graphically, o by optimization; [b] defined by Eq. (*9*); [c] criterion of agreement according to Eq. (*3*).

Correlation of Rate Constants with Solvent Parameters. In Table III are listed the average rate constants of the best four and eight parameter equations. These were used for correlation with properties of solvents presented in Table IV.

From division of the rate of butyric acid formation into two terms it becomes clear that the term corresponding to propagation reactions participates predominantly in the overall rate while the term involving initiation reaction is suppressed especially for acetonitrile and dimethylformamide.

Regression analysis was used to test the relation (*14*)

$$f(k) = af(I_s) + b\,, \tag{14}$$

where I is the solvent parameter; 99% and 95% probability of the linear relation was estimated with the use of tabelated values of critical correlation coefficients for the corresponding number of points in the set[32].

The effect of cohesion pressure of solvent. The cohesion pressure of butyraldehyde is higher (0·666 Pa) than the pressure of the product, butyric acid (0·568 Pa). According to Richardson and Soper[33], a solvent with higher cohesion pressure should exert rate-retarding effect, in agreement with the experiment (Fig. 2). If for theoretical description of the relation between reaction rate and the cohesion pressure of solvent a modified Laidler equation[17] is adopted, one can expect the validity of the proportionality

$$\ln k \sim (P_c)_s^{1/2}\,. \tag{15}$$

TABLE III

Values of Rate Constants of Best Equations (*1a*) and (*6a*)

Solvent	No	k_{1a} [a]	k'_{6a} [b]	k''_{6a} [c]
Acetonitrile	1	0·153	0 017	0·217
Butyraldehyde	2	0·199	1·013	0·152
Dimethylformamide	3	0·199	0·147	0·211
Ethyl acetate	4	0·435	6·204	0·220
Isooctane	5	0·725	8·545	0·435
Acetic acid	6	0·372	1·502	0·335
Dioxane	7	0·388	1·891	0·346
Chlorobenzene	8	0·459	2·269	0·391
n-Heptane	9	0·780	3·660	0·684
Toluene	10	0·502	4·650	0·445

[a] $\text{mol}^{1/2}\,\text{l}^{1/2}\,\text{h}^{-1}$; [b] $\text{mol}^{-1}\,\text{l}^{1}\,\text{h}^{-1}$; [c] $\text{mol}^{-1/2}\,\text{l}^{1/2}\,\text{h}^{-1}$.

TABLE IV

Physical Properties of Solvents Used for Correlation

Solvent	No	Refractive index n_D^{25} [a]	Viscosity η_{30} [a] Pa s	Fluidity f_{30} [d] kg m^{-3} . Pa^{-1} s^{-1}	Dipole moment μ_{25} [e] D, liq.	Cohesion pressure P_c [h] Pa
Acetonitrile	1	1·3416	3·25	237·2	3·39[f]	0·741
Butyraldehyde	2	1·3766	4·06[b]	194·9	2·45[g]	0·666
Dimethyl-formamide	3	1·4282	7·81[b]	120·3	3·86	0·819
Ethyl acetate	4	1·3698	4·00	222·2	1·83	0·488
Isooctane	5	1·3890	4·47	153·0	0	0·325
Acetic acid	6	1·3698	10·40	99·8	1·92[f]	0·682
Dioxane	7	1·4203	10·87	94·1	0·45	0·730
Chlorobenzene	8	1·5221[b]	7·15	153·2	1·23	0·686
n-Heptane	9	1·3851	3·64[c]	185·5	0	0·365
Toluene	10	1·4941	5·20	164·8	0·37	0·576

Solvent	No	Dielectric constant ε_{20} [a]	Solubility parameter δ [k] kJ$^{1/2}$ l$^{-1/2}$	Dimroth function E_{T30} [k] kJ/mol	Solubility of oxygen $V_S . 10^3$ [n] mol O$_2$ . . l$^{-1}_{solv.}$	Donor number DN [p] kJ/mol
Acetonitrile	1	37·5	23·9	193	—	59·0
Butyraldehyde	2	13·4[i]	18·6[l]	—	1·2[o]	—
Dimethyl-formamide	3	36·7[j]	24·1	183	4·91	111
Ethyl acetate	4	6·02[j]	18·2	160	8·88	71·6
Isooctane	5	1·94	18·8[l]	—	15·04	—
Acetic acid	6	6·15	18·2	214	—	—
Dioxane	7	2·21[j]	20·1	151	7·23	62·0
Chlorobenzene	8	5·62[j]	19·4	157	7·72	—
n-Heptane	9	1·92	15·1[l]	128[m]	14·10	—
Toluene	10	2·38[j]	18·2	142	9·01	0·4

[a] Ref.[25]; [b] interpolation; [c] ref.[26]; [d] calculated according to $f_{30} = d_{30}/\eta_{30}$; [e] ref.[27]; [f] 20°C; [g] 40°C; [h] calculated according to[28] $P_c = E_c/V^{1/3}$ where E_c is the total surface energy[25] (N m^{-1}), V is the molar volume[25] (m^3); [i] 26°C; [j] 25°C; [k] ref.[29]; [l] calculated according to[29] $\delta = (\Delta H_v/ /-RT)^{0.5}/V^{0.5}$ where ΔH_v is the enthalpy of evaporation at 25°C, R is the gas constant; [m] approximation to the CH_2 contribution; [n] ref.[30], at 0·1 MPA, 20—25°C; [o] approximated by the value for 2-methylpropanal at 30°C from ref.[31]; [p] ref.[16].

According to Table V this dependence is fulfilled for the rate constant of the four parameter equation on 99% probability level.

The greatest deviation from linearity is found for acetonitrile. The values for $(P_c)_s^{1/2}$ corresponding to hydrocarbons fulfill the linear dependence with 50% steepness. Constants of the eight parameter equation do not obey this dependece. In k' set one observes progressive decrease in $\ln k$(with increasing $(P_c)_s$).

The effect of viscosity of medium. Viscosity as the measure of "rigidity" of medium affects above all the reactions, the rate of which is controlled by the rate of diffusion of reactants to the distance required for their chemical interaction. In radical reactions the effect of viscosity could become apparent on comparing the rate of reaction conditioned by cage effect with the reaction requiring diffusion of radicals. According to approximative equation proposed by Bowen and Wokes[34] one can expect the validity of the following relation.

$$k \sim 1/\eta_s . \tag{16}$$

In our case, however, the dependence of this type has not been found. The products of self-termination (the role of cage effect) were not detected among reaction products. Similarly, the function of the viscosity-solvent fluidity ($f = \mathrm{d}/\eta$) does not fulfill this relation.

The effect of solvent polarity. Polarity of solvent plays a dominant role in influencing the course of ion reactions while the reactions between neutral species are affected to a substantially lesser extent. One of empirical characteristics of solvent polarity is the index of refraction n (of the properties included in the term polarity, it separates polarisability of the molecule). Its square is proportional to dielectric constant for nonpolar solvents which have not permanent dipole moment and for which n is determined at sufficiently long wavelength. According to Amis equation[17]

$$\ln k \sim 1/\varepsilon_s \tag{17}$$

and therefore

$$\ln k \sim 1/(n_D^2)_s . \tag{18}$$

In our case this relation is not fulfilled for the whole set of solvents but only for hydrocarbons of low polarity (maximum dipole moment 1·2 D, Fig. 3).

Another criterion of solvent polarity is the permanent dipole moment which expresses permanent charge distribution in the molecule. There is no straightforward relation between this characteristics and dielectric constant. In our case we observed the linear dependence for our set of solvents (Fig. 4) in the form

$$\ln k \sim \mu_s \tag{19}$$

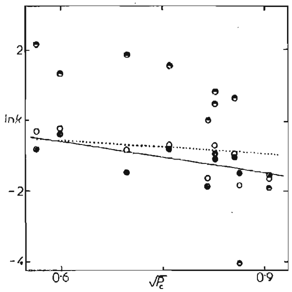


FIG. 2

Correlation of ln k_{1a} (solid line) with Cohesion Pressure of Solvent

Correlation coefficient $r = 0{\cdot}802$; the dependence for nonpolar solvents ($r = 0{\cdot}971$) is designated by dotted line; ○ values k_{1a}, ◓ k'_{6a}, ● k''_{6a}.

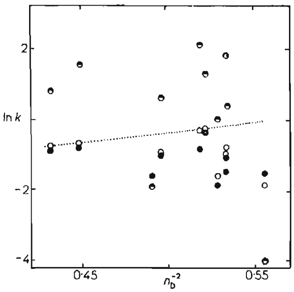


FIG. 3

Dependence of ln k on Refractive Index of Solvent

Dependence of k_{1a} for nonpolar solvents ($r = 0{\cdot}996$) is represented by dotted line; values k_{1a} ○, k'_{6a} ◓, k''_{6a} ●.

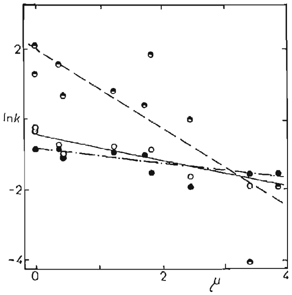


FIG. 4

Graph of Functions ln $k = a(\mu_s) + b$

○ k_{1a} values (solid line, $r = 0{\cdot}911$), ◓ k'_{6a} values (dashed line, $r = 0{\cdot}815$), ● k''_{6a} (dash and dot line, $r = 0{\cdot}820$).

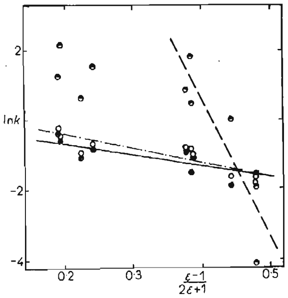


FIG. 5

Correlation of ln k with Kirkwood Function

○ k_{1a} values (solid line, $r = 0{\cdot}874$), ◓ k'_{6a} values (dependence for nonpolar solvents, dashed line, $r = 0{\cdot}874$), ● k''_{6a} values (dash and dot line, $r = 0{\cdot}836$).

TABLE V

Correlation Analyses of the Dependence of Oxidation Rate on Properties of Solvent $Y = aX + b$

Y	X	Correlation coefficient r^a	Slope a	Intercept b	$r/r_{\mathrm{krit.}}$
$\ln k_{1a}$	$(n_D^{25})^{-2}$	0·294	—	—	0·385
$\ln k_{1a}$	$(n_D^{25})^{-2b}$	0·996*	5·63	—3·21	1·006
$\ln k'_{6a}$	$(n_D^{25})^{-2b}$	0·623	7·36	—2·08	0·629
$\ln k''_{6a}$	$(n_D^{25})^{-2b}$	0·670	3·55	—2·44	0·677
k_{1a}	η^{-1}	0·118	—	—	0·154
k_{1a}	d/η	0·070	—	—	0·092
$\ln k_{1a}$	μ	0·911*	—0·36	—0·43	1·192
$\ln k'_{6a}$	μ	0·815*	—1·12	2·01	1·066
$\ln k''_{6a}$	μ	0·820*	—0·27	—0·74	1·073
$\ln k_{1a}$	$P_c^{0,5}$	0·802*	—3·92	2·03	1·049
$\ln k'_{6a}$	$\mathrm{P}_c^{0,5}$	0·672^d	—11·3	9·02	1·063^d
$\ln k''_{6a}$	$\mathrm{P}_c^{0.5}$	0·585	—2·34	0·65	0·764
$\ln k_{1a}$	$P_c^{0.5b}$	0·971*^{d}	—2·09	0·93	1·022^d
$\ln k_{1a}$	ε^{-1}	0·860*	2·36	—1·58	1·125
$\ln k'_{6a}$	ε^{-1}	0·692^d	6·55	—1·39	1·095^d
$\ln k'_{6a}$	ε^{-1c}	0·869^d	25·97	—3·23	1·071^d
$\ln k''_{6a}$	ε^{-1}	0·834*	1·88	—1·64	1·091
$\ln k_{1a}$	E_T	0·706	—0·012	1·10	0·846
$\ln k'_{6a}$	E_T	0·586	—0·041	6·85	0·702
$\ln k''_{6a}$	E_T	0·641	—0·010	0·40	0·768
$\ln k_{1a}$	$(\varepsilon - 1)/(2\varepsilon + 1)$	0·874*	—4·10	0·40	1·142
$\ln k'_{a}$	$(\varepsilon - 1)/(2\varepsilon + 1)$	0·718^d	—11·63	4·23	1·136^d
$\ln k'_{6a}$	$(\varepsilon - 1)/(2\varepsilon + 1)^c$	0·874^d	—38·44	15·89	1·077^d
$\ln k''_{6a}$	$(\varepsilon - 1)/(2\varepsilon + 1)$	0·836*	—3·23	—0·06	1·093
$\ln k_{1a}$	δ	0·782*	—0·16	2·10	1·023
$\ln k'_{6a}$	δ	0·827*	—0·58	11·56	1·082
$\ln k''_{6a}$	δ	0·584	—0·10	0·74	0·763
$\ln k_{1a}$	δ^2	0·781*	—0·005	0·51	1·021
$\ln k'_{6a}$	δ^2	0·851*	—0·014	5·93	1·113
$\ln k''_{6a}$	δ^2	0·564	—0·002	—0·27	0·737
k_{1a}	V	0·962*	45·27	0·08	1·153
k'_{6a}	V_S	0·770^d	480·62	—0·54	1·090^d
k''_{6a}	V_S	0·804^d	30·38	0·10	1·138^d
$\ln k_{1a}$	DN	0·559	—0·007	—0·74	0·583
$\ln k'_{6a}$	DN	0·401	—	—	0·418
$\ln k''_{6a}$	DN	0·760	—0·007	—0·85	0·793

[a] Values significant on 99% probability level are designated by asterisk; [b] only for hydrocarbons (toluene, isooctane, chlorobenzene, n-heptane); [c] without isooctane, toluene, n-heptane and dioxane; [d] 95% probability level.

with the greatest deviation of k' values for acetonitrile and dimethylformamide. The reaction rate increases with decreasing dipole moment, the rate contribution involving the ferrocene-catalysed initiation (k'_{6a}) decreasing more steeply.

The most important criterion of solvent polarity is the dielectric constant ε which is the measure of electrostatic effect of solvent. Its values represent macoprorperties of the medium and in a rough approximation they reflect the behaviour of the medium in the vicinity of the solvated reactant. For the rate dependence of the reaction of dipolar molecules, two basic equations have been proposed:

Amis equation[35]

$$\ln k = \ln k_r - 2\mu_1 \cdot \mu_2/kTr^3\varepsilon\,, \tag{20}$$

where k_r is the rate constant for the reference ε, μ are the dipole moments of reactants and r is the distance between both dipoles in the moment of reaction ($\boldsymbol{k}$ is Boltzman gas constant). This equation leads to the linear dependence (*17*).

Regression analysis of our set of solvents proved that this relation is fulfilled. The slope of the regression line is positive. The k'_{6a} constants are scattered, the points corresponding to toluene, n-heptane, isooctane and dioxane (maximum ε is 2·4) are located in one region without being dependent on $1/\varepsilon$ and the other solvents with higher ε fulfil the linear dependence, the slope of which indicates great sensitivity toward polarity changes. The greatest deviations are found again for acetonitrile (possible dielectric saturation) and dioxane (most likely due to specific solvation).

Laidler and Eyring[36] derived with the use of Kirkwood relation the equation which is valid for reactions in solvents with high dielectric constant, in which electrostatic forces prevail over nonelectrostatic contributions ϕ. For bimolecular reaction of *A* with *B* involving transition state Tr, the relation has the following form

$$\ln (k/k_o) = -(\varepsilon - 1)/\boldsymbol{k}T(2\varepsilon + 1)\,(\mu_A^2/r_A^3 + \mu_B^2/r_B^3 - \mu_{Tr}^2/r_{Tr}^3) + \Delta\phi/\boldsymbol{k}T\,. \tag{21}$$

Under the assumption of prevailing electrostatic contributions one can expect the validity of the following expression

$$\ln k \sim (\varepsilon_s - 1)/(2\varepsilon_s + 1)\,. \tag{22}$$

In our case Eq. (*22*) is valid for the rate constants of the first approximation (Fig. 5). A similar dependence has been found also for constants k''_{6a} (the main contribution by propagation reactions with chain transfer). In the case of k'_{6a} constants, the linear correlation is fulfilled only on 95% probability level. It has the greater steepness than k''_{6a}, the slopes being negative in both cases. The magnitude of the change in rate constants (k_{1a}) in the set of studied solvents is approximately equal to half order, which corresponds to literature data on radical reactions[15]. It further shows that propagation reactions of chain transfer predominate in the control of the process (initiation is not the rate determining step). However, k'_{6a} values vary by approximately 2·5 orders. As k'_{6a} constants include in the set of reactions also ion initiation reaction, their more pronounced dependence on the polarity of medium is easily understandable.

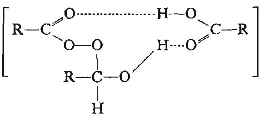
According to studies[7,9,11] solvent affects mainly propagation step 4. In the study[6] the relation (*22*) was used to identify the dipolar structure of transition state of propagation step for radical reaction

$$RCOOO^{\bullet} + RCHO \rightarrow [RCOOO : H^{-}RCO^{\bullet +}] \rightarrow RCOOOH + RCO^{\bullet} \quad \text{(step 4)}.$$

Also reported were solvent dependences of the rate constants of decomposition of radical initiators[9,14], propagation reactions of oxidation of cyclohexene[14], tetraline[8], styrene[6]. In all the cases mentioned the authors observed the dependence on Kirkwood function ε with positive slope. As our constants involve the constants of elementary reactions, starting from initiation up to carboxylic acid formation, one can expect that some ion steps are present in the overall reaction mechanism. The first ion step is the catalysed initiation reaction. We believe that this step involves oxidation of the aldehyde by the ferricenium ion formed by ferrocene oxidation (darkening of the solution of ferrocene in the initial stage of the reaction and partial discolouring after deactivation of samples of the reaction mixture by hydroquinone). This process leads to formation of a radical intermediate product. According to our evaluation, the oxidation of tetraline initiated by Co(II), Mn(II) and Cu(II) salts[8] have the positive slope of the dependence of ln k on the Kirkwood function (the correlation coefficient for *e.g.* Mn(II) salt is 0·799 for 12 solvents). All the dependences mentioned relate to the reactions in which – according to oxidation mechanism – the final product is equivalent to peracid in the oxidation of aldehydes. The consecutive ion process which has not been included into the correlated reaction rates is the bimolecular reaction of peracid with aldehyde to form carboxyl'c acid (step 7). It is assumed that this reaction is the main source of carboxylic acid[21,37]. This reaction is the sequence of two reactions which reversibly and at a substantially faster rate lead to formation of the complex of peracid with aldehyde (step 8) (for acetaldehyde[1], for butyraldehyde[38]) in some cases with catalytic participation of the carboxylic acid. This complex then decomposes in the rate determining step (step 9) to form the carboxylic acid.

$$RCOOOH + RCHO \rightleftharpoons RC(O)OOCH(OH)R \quad \text{(step 8)}$$

$$RC(O)OOCH(OH)R + RCOOH \longrightarrow$$



$$\longrightarrow 3\,RCOOH \quad \text{(step 9)}$$

Under our reaction conditions the conversion of the peracid into the acid was so fast that the former compound did not accumulate during the reaction, as confirmed by the analysis of the reaction mixture. Although the decomposition of the peracid is not the rate determining step of the whole oxidation process, with respect to the more polar character of step 7 and with regard to other radical reactions one can expect a certain induction of the sensitivity of the whole oxidation to changes in medium polarity. The negative slope of the ln *k* *vs* $(\varepsilon - 1)/(2\varepsilon + 1)$ dependence could indicate the decreased polarity in formation of the transition state of the reaction.

The effect of solubility parameter. Solubility parameter δ is defined[29] by Eq. (*23*), relates to cohesion pressure of liquids and is complementary to polarity

$$\delta^2 = (\Delta H_v - RT)/V, \qquad (23)$$

where ΔH_v is the molar heat of evaporation. Its relation to the reaction rate has been expressed by the expression[19]

$$RT \ln (k/k_0) = A\delta^2 + B\delta + C, \qquad (24)$$

where $A = \Delta V$ (the change in the molar volume on going to transition state), $B = -2\Delta(V\delta)$ and $C = \Delta(V\delta^2)$. For the reaction in which relatively nonpolar reactants interact to form relatively nonpolar transition state, *B* will be very small and one can write the following dependence

$$\ln (k/k_0) \sim \delta_s^2 . \qquad (25)$$

If transition state is more polar than the starting reactants then the following relation can be expected to be valid

$$\ln (k/k_0) \sim \delta_S . \qquad (26)$$

In our case the same satisfactory correlations were obtained for both dependences of ln k_{1a} on δ or δ^2 for the whole set of solvents (Fig. 6). The difference between these both dependences is statistically insignificant and the magnitude of the slope indicates very weak dependence on δ or δ^2. The k'_{6a} constant shows the close and steeper dependence with the negative slope (ΔV of the reaction is negative). The results of this correlation are consistent with correlations utilizing a function of ε which exhibited the closer correlation with k''_{6a} than with k'_{6a}. According to theory, good correlation of ln *k* on f(ε) suggests a weak dependence on f(δ) and *vice versa*.

From comparison of correlation coefficients (in relation to ε and δ, respectively) for constants k_{1a} (the whole reaction process) it seems more likely that the oxidation of butyraldehyde is affected by the polarity of medium rather than by nonelectrostatic contribution expressed by solublity parameter. Therefore one can assume the participation of ion step in the course of oxidation which would differ from initiation reaction (see also k''_{6a} values) and that would be likely decomposition of the peracid by the aldehyde. The greater change in k'_{6a} values due to solvents speaks rather for the participation of polar states compared to the sequence of reactions included in k''_{6a} constant. This agrees with the fact the k'_{6a} set contains further ion initiation reaction. On the other hand this contradicts with its closer correlation with δ values which could be expected rather for reactions not infolving distinct polar transition states. However, treatment of kinetic data reported by Russel[9] for the oxidation of cyclohexene initiated by AIBN or by Kamiyai[8] for the oxidation of tetraline initiated by Mn(II) decanoate reveal that both oxidations yield the correlation with solubility parameter (the correlation coefficient $r = 0{\cdot}9418$; $0{\cdot}8230$ respectively) which is equivalent to the correlation with Kirkwood function of ε (the correlation coefficient 0·8390; 0·7994). The difference in fitness of correlations with δ or $f(\varepsilon)$ is not here therefore conclusive concerning details on reaction mechanism.

Dependence on E_T function. Reichardt and Dimroth[39] proposed spectroscopically determined molar transition energy in a series of pyridinium N-phenylbetains as the

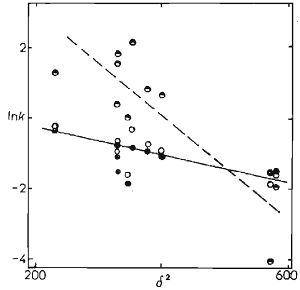


FIG. 6

Dependence of ln k on Square of Solubility Parameter of Solvent

○ k_{1a} values (solid line, $r = 0{\cdot}781$), ◒ k'_{6a} values (dashed line, $r = 0{\cdot}851$), ● k''_{a6} values.

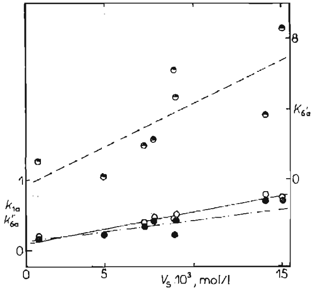


FIG. 7

Dependence of Rate Constants of the Oxidation on Solubility of Oxygen in Solvents Used (mol/l at 0·1 MPa and 25°C)

○ k_{1a} values (solid line, $r = 0{\cdot}962$), ◒ k'_{6a} values (dashed line, $r = 0{\cdot}770$) and ● k''_{6a} values (dash and dot line, $r = 0{\cdot}804$).

measure of the free energy of stabilization of ion pairs (the measure of the electrophilicity of solvent). The existence of dependence

$$\ln k \sim (E_T)_s \qquad (27)$$

indicates that transition state of the reaction has the structure similar to ion pair. In no case such correlations with E_T have been observed in our case.

The effect of donor number of solvent. As the measure of the donor ability of solvents we used DN values reported by Gutmann[16] which represent the enthalpy of coordination of a given solvent with $SbCl_5$. Again, the dependence (*28*) was not fulfilled in our case.

$$\ln k \sim (\mathrm{DN})_s \qquad (28)$$

Relation to solubility of oxygen in solvents. The higher solubility of oxygen in a given solvent will increase the concentration of oxygen in the liquid phase which is available for the reaction. We found that k_{1a} can be correlated with $(V_S)_s$ (Eq. (*29*)); the rate constant

$$k_{1a} \sim (V_S)_s \qquad (29)$$

increases with increasing concentration of oxygen in the liquid phase (Fig. 7). Dependence of the rate constant on the concentration of dissolved oxygen was included *e.g.* into constant k_{1a} by its definition (Eq. (*7*)).

For constants of the eight parameter equation this dependence is not valid on 99% probability level. In this case, however, a substantially greater increase in k'_{6a} constants compared to k''_{6a} with increasing concentration of dissolved oxygen is remarkable. From the difference in the slopes one can expect that the reaction order in oxygen will be higher for rate term with k'_{6a} than for the term with k''_{6a}.

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