STUDY OF THE CORRELATION BETWEEN STRUCTURE AND REDUCIBILITY OF ACETOPHENONE DERIVATIVES

I. THE VALIDITY OF THE HAMMETT EQUATION IN THE MEERWEIN—PONNDROF—VERLEY REDUCTION OF ACETOPHENONE DERIVATIVES

By

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Introduction

The correlation between the structure and reactivity of ring substituted aromatic compounds has been the subject of several investigations [1—4]. The first quantitative relationship was given by Hammett [1] who proved the validity of his equation for 57 different reactions. The equation is best known in the following form:

$$\log \frac{k}{k_0} = \sigma \varrho \qquad (1)$$

where k is the rate constant in a certain reaction of the ring substituted derivative,

k_0 is the rate constant in the same reaction of the unsubstituted derivative,

σ is a constant characteristic of the substituent and

ϱ is a constant characteristic of the reaction.

Later Jaffe [2] found that Eq. (1) is valid for more than 200 reactions, but the study of further reactions revealed the lack of general validity of Hammett's equation. It was assumed that this was due to the fact that the values of the substituent constants as determined by Hammett were not the same for all reactions. This led to the introduction of modified substituent constants for certain reactions [3] and to the modification of the original equation [4].

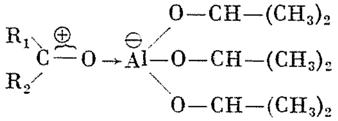
There is but little reference in the literature on the validity of the Hammett equation for reduction processes [5—10]. Both homogeneous and heterogeneous catalytic reactions were studied on various model substances. When reducing substituted nitrobenzenes in the homogeneous phase with $TiCl_3$ or with $SnCl_2$, Kindler [5] and Agata and Sugiyama [6], respectively found that the Hammett equation was only approximately valid. Franzen [7] reduced substituted phenylhydrazones also in the homogeneous phase with $SnCl_2$ and found that in this case Hammett's equation was not valid.

The Hammett equation was found again invalid by Roe and Montgomery [8] for the heterogeneous reduction of Schiff's bases when catalyzed with PtO_2 and by Hernandez and Nord [9] for the rhodium catalyzed heterogeneous reduction of aromatic nitro compounds. On the other hand, Smonyina [10] established the validity of the Hammett equation in the Pt on charcoal catalyzed reduction of nitrobenzene derivatives.

In our earlier work we have investigated the activity of various metal catalysts in liquid phase reactions [11]. As a continuation of this work it seemed interesting to search for a correlation between the structure of the substrata and their behaviour in catalytic processes. It appears from the pertaining literature that the simple relationships which were found valid for various reactions in the homogeneous phase are by no way directly applicable to catalytic processes in the heterogeneous phase. We have therefore attempted a comparison of the reduction processes on the same substrata in homogeneous and heterogeneous phases, that is to say we tried to find correlations equally valid for homogeneous and heterogeneous phase reactions.

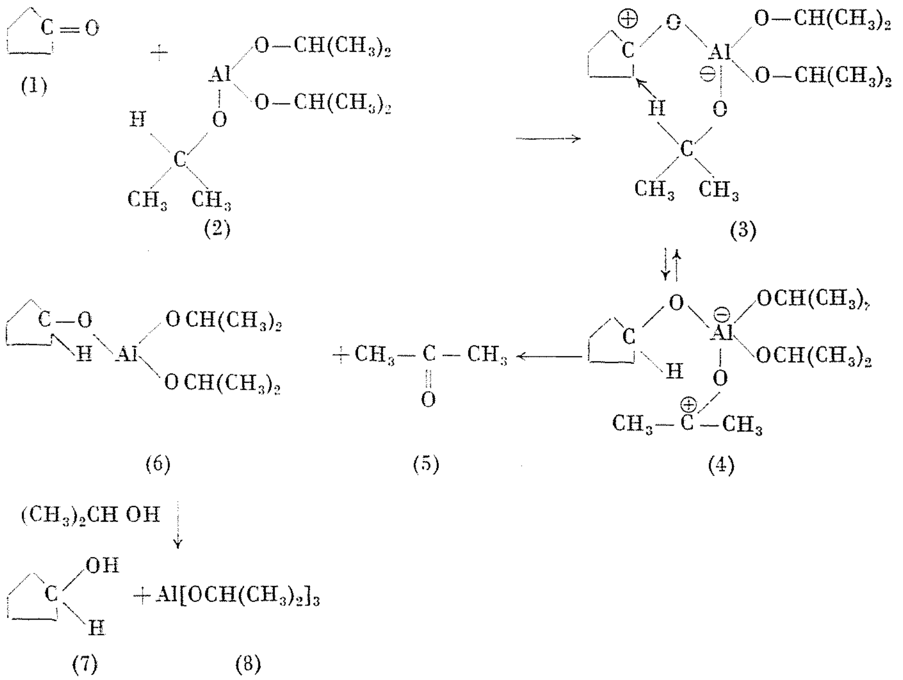
As a model for the study of the relationship between chemical structure and reactivity the reactivities of meta and para substituted acetophenone derivatives in the Meerwein—Ponndorf—Verley (in the following M—P—V) reduction were chosen. This choice is partly justified by the fact that this reaction is selective for the carbonyl group so that the effect of other reducible substituents (e.g. $-NO_2$, $-COOCH_3$) can also be studied, while the mechanism of this reaction has been repeatedly investigated [12—21] so that in spite of some still existing problems this field can be considered as more or less elucidated.

Meerwein [12] already supposed a coordination complex structure for the intermediate product of the reaction, which is in agreement with later conceptions on the progress of the reaction [18]. Thus a coordination compound is formed from 1 mole of aluminium oxide and 1 mole of ketone:



$$\begin{array}{l} \qquad\qquad\qquad O-CH-(CH_3)_2 \\ \begin{matrix}R_1\\R_2\end{matrix}\!\!>\overset{\oplus}{C}\overset{-}{=}O\rightarrow\overset{\ominus}{Al}-O-CH-(CH_3)_2 \\ \qquad\qquad\qquad O-CH-(CH_3)_2 \end{array}$$

The complex is stabilized by the cleavage of a hydride (H^-) anion which is then bound by the carbonium carbon atom of the oxo compound. In the reduction of cyclopentanone with aluminium isopropylate the hydride anion is bound by the oxo carbon atom of the cyclopentanone after which acetone is split off from the complex and a mixed alcoholate of cyclopentanol and isopropanol is formed.



The complex formed in the first step of the reaction (3) fulfils simultaneously two functions:

1. it associates and arranges the reaction partners into such a favourable steric order that steric interaction will be the lowest;

2. by way of the coordination between the aluminium ion and the oxygen of the carbonyl group the positive charge on the carbonyl carbon atom is enhanced whereby the hydride ion will be bound more readily.

Recent investigations have established the reaction order and the rate controlling step of the reaction.

According to the literature the reaction proceeds in four steps (complex formation, migration of the hydride ion, cleavage of the oxidized form of the reducing agent from the complex and the formation of the reaction end-product by transesterification of the mixed alkoxide). No agreement has been reached with respect to the rate controlling step; some of the authors maintain that the second, others that the fourth step is the rate controlling one. The reduction was found of the first order for the ketone (assuming that the fourth step is the rate controlling one), of the 1.5th [19], i.e. of the 2nd [21] order for aluminium isopropylate (assuming that the second step is the rate controlling one).

A further complication is introduced into this pattern by the fact that the reacting aluminium alkoxide may react in dimeric, trimeric or tetrameric form, so that during the reaction the concentration of the active form of aluminium alkoxide cannot be considered constant [21].

Experimental

The M—P—V reduction of 16 ring substituted acetophenone derivatives was studied. The model compounds were the following:

m-NO_2 acetophenone
m-NH_2 acetophenone
m-OH acetophenone
m-OCH_3 acetophenone
m-Cl acetophenone
m-Br acetophenone
m-$N(CH_3)_2$ acetophenone
m-CN acetophenone
m-COOH acetophenone
m-$COOCH_3$ acetophenone
p-NO_2 acetophenone
p-NH_2 acetophenone
p-OH acetophenone
p-OCH_3 acetophenone
p-Cl acetophenone
p-Br acetophenone

These acetophenone derivatives were reduced with aluminium isopropylate in isopropylalcohol solvent at boiling temperature under continuous removal of the acetone formed.

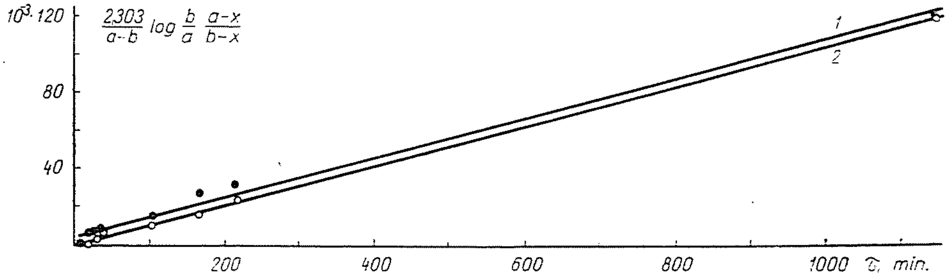


Fig. 1

The progress of the reaction can be followed up by the determination of the concentration changes of the initial substances or of the end product. Magnetic nuclear resonance measurements [21] have indicated that in the M—P—V reduction of acetophenone the total quantity of unreacted acetophenone plus formed acetone is always 100% throughout the entire reaction process. Evaluation of the infrared absorption spectra (measured by the Spectroscopic Group of the Hungarian Academy of Sciences) has led to a similar result (Fig. 1). Thus the progress of the reaction can be followed by measuring either the concentration of the acetophenone or the quantity of the acetone formed. With a view to these facts calculation of the reaction rates was based on the determination of the quantity of acetone at given intervals.

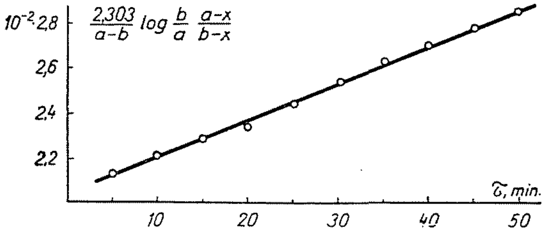


Fig. 2

The quantity of acetone formed was determined iodometrically [22] in the distillate. Under these experimental conditions the net reduction process was found to be of the second order from both infrared spectroscopic measurements and from the quantity of acetone which had been removed from the

Table I

Rate constants of the Meerwein—Ponndorf—Verley reduction of acetophenone derivatives

No.	Substituent	Hammett	$k \cdot 10^2$	$\log k$
1	p-OH	−0.357	0.91	−2.0419
2	p-OCH_3	−0.268	1.10	−1.9586
3	m-$N(CH_3)_2$	−0.211	1.03	−1.9847
4	p-CH_3	−0.069	1.32	−1.8891
5	m-OH	−0.002	1.61	−1.7744
6	H—	0	1.83	−1.7375
7	m-OCH_3	+0.115	1.90	−1.7213
8	p-Cl	+0.227	1.93	−1.7151
9	p-Br	+0.252	2.06	−2.6861
10	m-$COOCH_3$	+0.315	0.96	−2.0172
11	m-COOH	+0.345	1.01	−2.0022
12	m-Cl	+0.375	2.97	−1.5272
13	m-Br	+0.391	2.60	−1.5849
14	m-CN	+0.678	1.25	−1.9045
15	m-NO_2	+0.710	1.39	−1.8567
16	p-NO_2	+0.778	1.78	−1.7496

reaction mixture by distillation (Figs 1 and 2). For reactions of the second order

$$\frac{dx}{dt} = k(a - x)(b - x) \tag{2}$$

After separation, arrangement, integration and logarithmation of the variables

$$2.303 \lg (a - x) - \lg (b - x) - \lg \frac{a}{b} = (a - b) kt \tag{3}$$

is obtained where a and b are the initial concentrations of the reactants, x is the converted quantity (in mole per litre) up to time t, k the rate constant of the reaction and t the time (in minutes). The k values calculated from Eq. (3) are summed up in Table I.

Discussion

The reduction rate of 16 meta and para substituted acetophenone derivatives in the Meerwein—Ponndorf—Verley reaction was measured. The rate constants of the reduction processes were determined (Table I).

The validity of Hammett's equation for this reaction was examined by substituting the rate constants into Eq. (1.) Plotting the logarithm of the rate constants *vs* Hammett's σ constant which should be characteristic of the substituents the points obtained can be joined not by one but by two straight lines (Fig. 3*a*). On one of the lines (I) points corresponding to acetophenone derivatives which contain primary substituents, on the second line (II) points corresponding to acetophenone derivatives with secondary substituents can be fitted. The slopes of the two lines were determined from the principle of least squares. The values of the Hammett reaction constants (ϱ) are then

$$\text{for line I: } \varrho_{\text{I}} = -0.298$$
$$\text{for line II: } \varrho_{\text{II}} = -0.275$$

The difference between these two values is within the limits of error of the calculation method and the values can be regarded as practically identical. A similar result is obtained upon replacing the original Hammett substituent constants by the σ^+ values introduced by OKAMOTO and BROWN [3] (Fig. 3*b*).

It follows from the aforesaid that Hammett's equation is not valid for the M—P—V reduction of acetophenone derivatives. According to literature data Hammett's equation was either invalid [7, 8] or only approximately valid [5, 6] for the reduction of other compounds (e.g. aromatic nitro and quinone derivatives) both in the homogeneous and in the heterogeneous phase. The latter authors [5, 6] studied the effect of only few secondary substituents which prevented them to notice the difference found by us with substituents.

Our results may be summed up in stating that in the M—P—V reduction of acetophenone derivatives neither the original (σ) nor the modified (σ^+) substituent constants are applicable. If, however, the effects of the primary and secondary substituents are studied separately, then by using either the original (σ) or the modified (σ^+) Hammett substituent constants two practically parallel straight lines are obtained which are well fitted by the points obtained with primary and secondary substituents, respectively.

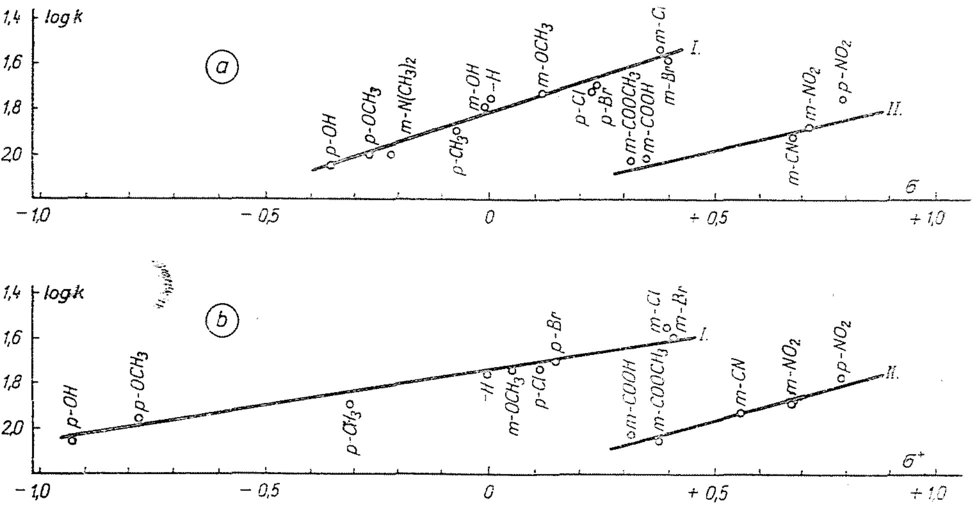


Fig. 3

Experimental method

The experiments were carried out in the apparatus shown in Fig. 4. 0.1 mole of acetophenone or one of its derivatives (whose melting and boiling points agreed with literature data) was weighed into a round bottomed flask *1* and dissolved in 100 ml of anhydrous isopropylalcohol [23]. Six millilitres of methylalcohol were poured into the evaporator of column *2*, the ground joints adjusted and the flask immersed in an oil bath at 110° C. Water at 67° C was circulated in jacket *3*. As soon as the parts of the apparatus had reached the desired temperature, a hot solution at 80° C, 12.2 g (0.18 gramequivalent) of freshly distilled aluminium isopropylate in 60 ml of anhydrous isopropylalcohol was added from tank *6* to the contents of flask *1*. The appearance of the first drop of distillate at the end of condenser *4* was considered as the beginning of the reaction. Depending on the quantity of the distillate the receivers *5* were changed every 5 to 10 minutes. The reaction was continued up to the collection of 8—10 samples.

In the evaluation of the infrared absorption bands the progress of the reaction was followed through the intensity decrease of the 1694 and 1273 cm^{-1} bands of acetophenone and the intensity increase of the 1713 cm^{-1} band of acetone. The concentrations of the initial and end products were determined with the help of the previously prepared acetophenone—acetone calibration curve. Into the reference cell (0.04 mm thick layer) isopropylalcohol used as solvent was poured. At $t = 0$ the concentration of acetophenone was 0.5555 mole per litre, and of aluminium isopropylate 1 gramequivalent per litre.

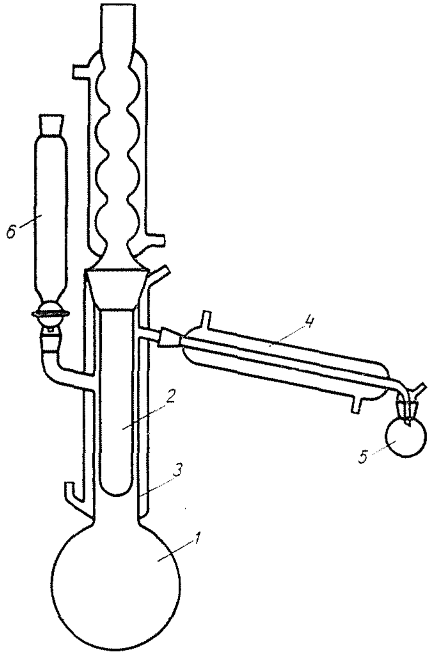


Fig. 4

Summary

The reaction rates in the Meerwein—Ponndorf—Verley reduction of 16 meta and para substituted acetophenone derivatives were measured. The net order of the reaction is 2. The effect of the substituents cannot be characterized either by the original or by the modified variations of Hammett's equation.

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STUDY OF THE CORRELATION BETWEEN STRUCTURE AND REDUCIBILITY OF ACETOPHENONE DERIVATIVES

II. PHYSICAL PROPERTIES AND REACTIVITY

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Introduction

The correlation between the structure and reactivity of ring substituted aromatic compounds has been the subject of several investigations which revealed a number of qualitative and quantitative relationships [1—3], there are, however, only few studies dealing with reduction processes from this aspect and even these contain contradictory data [4—9].

In our previous communication [16] the reaction rates of meta and para substituted acetophenone derivatives in the Meerwein—Ponndorf—Verley reduction have been described and the fact was established that the Hammett equation is not valid either in its original or modified form for these rate constants. We have therefore embarked on the measurement of those properties of the earlier investigated acetophenone derivatives which are characteristic of their physical structure and which may be related to their chemical reactivity.

Literature

There are some literature data which indicate a correlation between the reaction rate constants and certain physical parameters (e.g. redox potential, exaltation, polarization forces) [10—15].

Redox potential. — Dimroth [10] studied the correlation between the redox potential and the rate constant in the reduction of quinone derivatives in the homogeneous phase (organic reducing agent) and found the logarithm of the reduction rate to be proportional to the redox potential. For two different quinone derivatives:

$$\log k_2 - \log k_1 = m\,(E_2 - E_1)$$

where m is a proportionality factor, E_1 and E_2 are the redox potentials of the two derivatives and k_1 and k_2 are the rate constants of the reduction process. There was almost no difference in the values of the proportionality factor m in the various series.

According to PREISLER [11], the $-CH_3$, $-OH$, $-NH_2$, $-OCH_3$, $-NH-CH_3$, $-N(CH_3)_2$, $-NH-C_6H_5$ groups reduce, while the $-SO_3H$, $-COOH$, $-COOC_2H_5$ groups and the halogenides enhance the redox potential of aromatic compounds.

Exaltation in molar refraction. — The difference between experimentally determined and calculated molar refraction is called exaltation. This exaltation is characteristic of the molecular structure and is therefore a valuable tool in the study of the structure of chemical compounds [9].

CURRAN and PALERMOTTI [13] have studied the polarization engendered by electron donor and acceptor groups in aromatic compounds and measured molar refraction in benzene solutions with the sodium D line as reference line. They found from the difference between the measured and calculated values (exaltation) that the greater the possibility of mesomery in the compound the higher will be the value of exaltation.

PALOMA [14] investigated the acid hydrolysis of the ethyl ester of acetoacetic acid, β-methoxy-propionic acid and of β-oxypropionic acid in aqueous solutions at 25° C and found that the measured rate constants vary in opposite order than do the atomic refractions of oxo, ether and hydroxyl oxygen.

The polarization force engendered by the substituent. — PRICE [15] used the polarization force to characterize the strength of the electrostatic forces within the molecule.

The electrostatic force which acts on the π electrons in the double bond neighbouring the selected atom can be calculated on a suitably chosen model. For phenol the calculation is the following:

$$\text{Polarization force} = \frac{-2.18}{1.89^2}\cos 41.1^\circ + \frac{1}{2}\,\frac{1.58}{2.15^2}\cos 68.8^\circ + \\ + \frac{1.58}{2.61^2}\cos 24.5^\circ \times 4.77 \times 10^{-4} = -1.46 \times 10^{-4}\,\text{dyn}$$

that is to say an electrostatic force of -1.46×10^{-4} dyn acts on the π electrons of the double bond adjacent to the OH group.

The bond distances and bond angles necessary for the calculation were obtained from X-ray and electron diffraction measurements. The bond moments were calculated from the dipole moments.

There is a quantitative correlation between the polarization forces and Hammett's σ constants.

Experimental

The reaction rate of ring substituted acetophenone derivatives in the Meerwein—Ponndorf—Verley reduction and the redox normal pontential, molar refraction and infrared C=O frequency of the model compounds were measured, the exaltation of molar refraction was claculated and a correlation was sought between these parameters and Price's polarization forces [15] as well as the Hammett constants.

The following acetophenone derivatives were included in the experiments:

m-NO_2 acetophenone
m-NH_2 acetophenone
m-OH acetophenone
m-OCH_3 acetophenone
m-Cl acetophenone
m-Br acetophenone
m-$N(CH_3)_2$ acetophenone
m-CN acetophenone
m-COOH acetophenone
m-$COOCH_3$ acetophenone
p-NO_2 acetophenone
p-NH_2 acetophenone
p-OH acetophenone
p-OCH_3 acetophenone
p-Cl acetophenone
p-Br acetophenone

The method for the determination of the reaction rate and of the rate constant was described in the previous communication [16].

Measurement of the redox potential. — The redox potentials were determined in the equimolar mixture of the acetophenone derivatives with their corresponding reduced derivatives in isopropylalcoholic solution at the boiling point of the solvent.

The redox process controlling the potential is the following:

$$\phi-CO-CH_3 + 2H^+ + 2e^- \rightleftharpoons \phi-CH(OH)-CH_3$$

The redox potential is:

$$E = E_0 + \frac{RT}{zF} \ln \frac{[ox]}{[red]}$$

where E_0 is the normal potential of the redox system
T is the absolute temperature
[ox] is the concentration of the corresponding ketone
[red] is the concentration of the corresponding alcohol.
E can be measured with a suitable reference electrode.

Calculation of molar refractions and exaltations. The electron polarization (P_e) molar refraction (R_M) of a given molecule can be calculated from the Mosotti—Clausius equation:

$$P_e \equiv R_M = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{d}$$

where n is the index of refraction of the substance, d its density (at the same temperature) and M its molecular weight; n and d can be determined experimentally.

Molar refraction can also be calculated in another way, namely from the known refraction values of atomic bonds within the molecule [19]; molar refraction is the sum of these refraction values.

There is a difference between the molar refraction values obtained from the measurement of the refractive index and calculated from the Mosotti—

Table I

Measured redox potentials, molar refractions, rate constants in the M—P—V reduction and infrared C=O frequencies of substituted acetophenone derivatives

Substituent group	Redox normal potential	$R_{M,sb}$ calc.	R_M meas.	E_x	$k \times 10^2$	Hammett σ	cm^{-1} ν
-H	205	—	—	—	1.83	—	1687
m-NO_2	220	—	—	—	1.39	+0.710	1697
m-NH_2	—	—	—	—	—	—	1672
m-OH	155	37.29	38.83	0.0396	1.61	—0.002	1667
m-OCH_3	125	42.07	42.95	0.0205	1.90	+0.115	1689
m-Cl	245	40.46	41.29	0.0205	2.97	+0.375	1695
m-Br	260	43.34	45.03	0.0374	2.60	+0.391	1695
m-$N(CH_3)_2$	15	48.64	52.37	0.0730	1.03	—0.211	—
m-CN	90	—	—	—	1.25	+0.678	1695
m-COOH	95	—	—	—	1.01	+0.345	1693 1662
m-$COOCH_3$	105	46.61	47.76	0.0240	0.96	+0.315	1687
p-NO_2	175	—	—	—	1.78	+0.778	1695
p-NH_2	—	—	—	—	—	—	1655 1645
p-OH	—	37.29	38.65	0.0959	0.91	—0.357	1652
p-OCH_3	160	42.07	44.01	0.0440	1.10	—0.268	1680
p-Cl	190	40.46	41.62	0.0279	1.93	+0.227	1692
p-Br	210	43.34	44.59	0.0276	2.06	+0.232	—
p-CH_3	130	40.29	41.48	0.0268	1.32	—0.069	1684

Table II

Changes in the physical parameters of acetophenone derivatives and the Price polarization forces

Substituent group	P dyn × 10^4	$\log \frac{k_{\mathrm{para}}}{k_{\mathrm{meta}}}$	$E_p—E_m$ mV	$\nu_p—\nu_m$ cm^{-1}	$Ex_p—Ex_m$
$—NH_2$	−1.66	—	—	−27	—
—OH	−1.46	0.2675	−115	−15	+0.0199
$—OCH_3$	−1.21	0.2373	+ 35	− 9	+0.0135
—Cl	−0.68	0.1879	− 55	0	+0.0074
—Br	−0.55	0.1012	− 50	—	−0.0098
—H	+0.45	0.0000	—	0	0.0000
$—NO_2$	+2.21	−0.1071	− 45	0	—

It was not possible to measure the reaction rates and redox potentials of acetophenone derivatives containing amino groups because of the condensation reaction between the amino and the acetyl groups at higher temperatures. The reason for the other lacking data is the smallness of samples which were available from some of the compounds.

Clausius law ($R_{M,m}$) and the molar refractions calculated as the sum of bond refractions ($R_{M,sb}$). This exaltation can be brought into relation with the structure of the molecule. Exaltation (E_x) is

$$E_x = \frac{R_{M,m} - R_{M,sb}}{R_{M,m}}$$

The values of the indices of refraction (n) and of the density (d) which are necessary for the calculation of molar refractions and exaltations were measured with the Zeiss—Abbé refractometer [17] and the pyknometer [18], respectively, at temperatures above the melting points of the substances (between 25 and 55° C).

The spectra of the acetophenone derivatives were measured by the Spectroscopic Group of the Hungarian Academy of Sciences in the liquid (film) or in the solid (tablet) state.

The values of the Price polarization forces (P) were taken from the literature [15].

The results of the measurements are summed up in Tables I and II.

Results and discussion

The reaction rate in the Meerwein—Ponndorf—Verley reduction, the redox potential, molar refraction, the exaltation of the molar refraction and the infrared C=O frequencies of 16 meta and para substituted acetophenone derivatives were determined. The results are summed up in Table

I. A correlation between these parameters as well as the Price polarization forces and the Hammett constants (σ) was sought.

A direct proportionality was found between the logarithms of the reduction rate constants and the redox normal potential (Fig. 1), in agreement with the results obtained by DIMROTH [10].

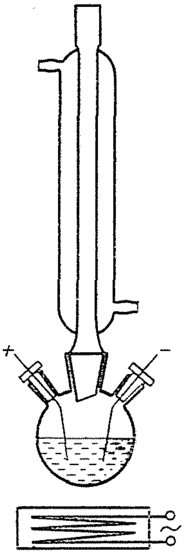

Fig. 1

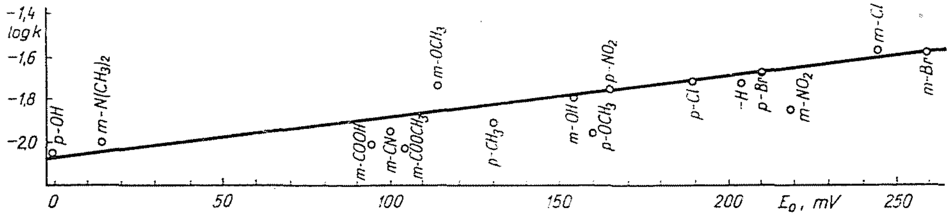

Fig. 2

A correlation was sought between the other physical parameters measured and the rate constants, i.e. the Hammett and Price constants in different variations. A relatively simple correlation was found only for those acetophenone derivatives for which both the para and meta substitutions were available. In these cases the differences of the investigated parameters (redox potential, infrared C=O frequency, exaltation of the molar refraction, logarithm of the rate constant of the Meerwein—Ponndorf—Verley reduction) *vs* the polarization forces gave curves of similar shapes (Fig. 2). The curves show a steep decline in the region of negative polarization, while for positive polarization forces the ordinate values change but slightly (or have a limiting value) which shows that there is little or no difference between certain parameters of the para and meta derivatives. Thus the logarithms of the quotients of the rate constant of the para and meta derivatives decrease linearly while the values of the Price polarization constants which are characteristic of the substituent change from the negative direction to a value of approximately +0.5. Further experiments are needed to decide whether the correlation is generally valid for other reduction processes, too.

Experimental method

Measurement of the redox potential. — The redox potentials were measured in the apparatus shown in Fig. 3. 0.05 mole of acetophenone (or its derivative) and 0.05 mole of its reduced product were weighed into a 25 ml three-necked

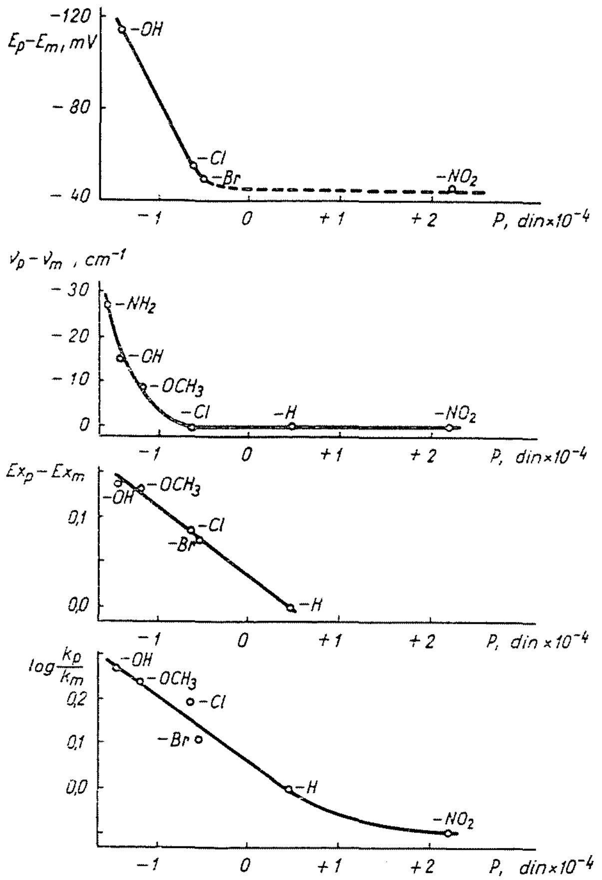

Fig. 3

round bottom flask. (The reduced products were isolated from the reaction mixture of the Meerwein—Ponndorf—Verley reduction [16], their melting or boiling points agreed with the literature data.) Nine millilitres of anhydrous isopropylalcohol were now added and the flask joined to a reflux condenser. The apparatus was placed over a hot plate and its contents boiled for a few minutes. Pt and Ag/AgCl electrodes were immersed then into the solution and the electromotive force of the system was measured with a Radelkisz Op 201 type instrument. The measurements were performed at 82.5° C, the temperature of the boiling point of the solution.

Infrared spectroscopy. — The spectra of the acetophenone derivatives were tested in the liquid (film) or solid (KBr tablet) state of the substance with a Zeiss UR-10 type channel infrared spectrograph, with a slit program 4, at 50 cm^{-1} min recording rate, needle mobility 50, amplification 2, band width 2, retardation 2.

Determination of molar refractions. — In the pertaining Tables only some of the necessary *n* and *d* values occurred, so that all indices of refraction and densities were experimentally determined. To check the accuracy of the measurements wherever possible we compared our own data with the values in the literature. (There was a satisfactory agreement between our own values and the literature data.)

The indices of refraction of the acetophenone derivatives were measured in visible light with the Zeiss—Abbé refractometer (50); of the liquids at 25° C, of the solids at 1—2° C above their melting point.

The density of the model compounds was determined with the pyknometer.

Summary

A correlation was sought between the rate constants of meta and para substituted acetophenone derivatives in the Meerwein—Ponndorf—Verley reduction and certain physical parameters of the model compounds which are characteristic of their structure. The redox potential (under the conditions of reduction), and the molar refraction of the model compounds were measured, the exaltation of molar refraction was calculated, and the infrared C=O frequency measured and a correlation was sought among these parameters. A relatively simple correlation was found only when the physical parameters and the logarithms of the rate constants of the model compounds were plotted as functions of the Price polarization forces.

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