European Polymer Journal, 1972, Vol. 8, pp. 1237–1246. Pergamon Press. Printed in England.

THE KINETICS OF RADICAL POLYMERIZATION—XXV

STUDY OF THE RADICAL REACTIVITY OF SUBSTITUTED NITROBENZENES—I

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(*Received* 28 *February* 1972)

Abstract—A study was made on the effect of some *para*- and *meta*-substituted nitrobenzenes on the radical polymerization of vinyl acetate. It has been shown that $-CH_2X$ and $-SO_2X$ type substituents have merely an inductive effect on the reactivity of nitro groups. It has also been established that the inductive effect of substituents is more intensive when they are in the *para* position than when in the *meta* position, i.e.: $\lambda = 1{\cdot}15$.

The ρ constant characteristic of the reaction between poly(vinyl acetate) radicals and substituted nitrobenzenes was found to be $+1{\cdot}05$.

IT IS KNOWN that *meta*- and *para*-substituted benzene derivatives serve as important model systems for investigations dealing with the influence of structure on reactivity. In the first stage of these investigations, the substituent constants (σ), introduced by Hammett and presumed to be independent of the reaction centre of the above compounds,[1,2] have been applied for the quantitative description of the electronic structure. With an increase of the experimental data, however, it turned out that several reactions of *para*- and *meta*-substituted benzene derivatives cannot be fully described with these constants [see e.g. refs. [3–7]]. Although the introduction of further constants [σ^+, σ^-[4–8] σ^0[9]] for the different reaction types led to better results, it was soon evident that no universal series of substituent constants (suitable for the description of any type of reaction) can be set up. Recently, there have been several approaches to the problem of determining quantitatively the inductive and mesomeric effects of the substituents and specifying the inductive ($\pm I$) and mesomeric ($\pm M$) parts of the total effect of the substituent.[10–16] These researches were chiefly based on Taft's concept, by which the total effect of the substituent is made up by the addition of independent mesomeric and inductive effects.

Based on the above consideration and the results of further investigations, the Hammett constants may be given as[11,16–18]:

$$\sigma_p = \lambda\sigma_I + \sigma_R \tag{1}$$

and

$$\sigma_m = \sigma_I + \alpha\sigma_R, \tag{2}$$

where σ_I and σ_R are inductive and mesomeric components of the substituent constants, while λ and α stand for the relative intensities of the inductive and mesomeric effects in the cases of *para*- and *meta*-substitution of the benzene ring, respectively.

The purpose of our present study was to examine closely the applicability of the above equations for radical reactions. According to the literature, only a few radical reactions have been studied from this aspect; further, the studies of the substituent effect in each case involved only a few substituents. Therefore, the data at present

available are insufficient to decide whether radical reactions can be satisfactorily described by the Hammett equation or whether the substituent constants derived from radical reactions may be discussed by the additive scheme according to (1) and (2), and if so, how great are the inductive or mesomeric effects.

For this purpose, a study was made on the effects of many *para-* or *meta*-substituted nitrobenzenes on the initiated polymerization of vinyl acetate. Literature data[20,21] led to the conclusion that mono-substituted nitrobenzenes behave as inhibitors in the radical polymerization of this monomer. Owing to the low reactivity of vinyl acetate monomer, only inhibition is to be expected in this system, making possible the precise determination of the relative reactivities of *para-* and *meta-* substituted nitrobenzenes.

In this communication, we report studies of the radical reactivities of *para-* and *meta*-substituted nitrobenzenes for which, to a first approximation, the substituent exerts only an inductive effect on the reaction centre.

EXPERIMENTAL

Polymerization kinetic measurements were performed dilatometrically; this procedure and the purifications of the initiator (AIBN) and vinyl acetate have already been described in detail.[22] The nitro compounds were prepared as follows:

Nitrobenzene: analytically pure material was distilled *in vacuo*; $n_D^{20} = 1{\cdot}5529$.

3-*Nitrobenzyl chloride:* 3-nitrobenzyl alcohol was reacted with phosphorus pentachloride; the product was recrystallized three times from petroleum ether ;[23] m.p.: 46°.

4-*Nitrobenzyl chloride:* the product from the reaction of 4-nitrobenzyl alcohol and thionyl chloride was recrystallized three times from petroleum ether: m.p.; 71°.

3-*Nitrobenzyl bromide:* was obtained from a pss. grade product (Fluka AG.) by recrystallization from petroleum ether; m.p.: 57–58°.

4-*Nitrobenzyl bromide:* was prepared from a Fluka AG. product (purity: pss.) by recrystallization from petroleum ether; m.p.: 99–100°.

3-*Nitrobenzyl cyanide:* an aqueous solution of potassium cyanide in alcoholic medium was reacted with 3-nitrobenzyl chloride.[24] The product was recrystallized several times from a mixture of ligroin and ether; m.p.: 61–62°.

4-*Nitrobenzyl cyanide:* a product of Fluka AG. (purity: pss.) was recrystallized twice from ethyl alcohol; m.p.: 115–116°.

3-*Nitrophenyl nitromethane:* was prepared by the reaction of silver nitrite with 3-nitrobenzyl chloride in benzene–ether mixture;[25] the product was recrystallized three times from ethyl alcohol; m.p. 94–95°.

4-*Nitrophenyl nitromethane:* was produced by the reaction of silver nitrite with 4-nitrobenzyl iodide in an alcoholic medium,[26] and then recrystallized three times from ethyl alcohol; m.p.: 91°.

3-*Nitrobenzyl acetate:* was synthesized by the reaction of 3-nitrobenzyl alcohol with acetic anhydride. The product was then distilled *in vacuo*; b.p.: 161–163°/20 torr, m.p. 36°.

4-*Nitrobenzyl acetate:* was prepared from 4-nitrobenzyl alcohol and acetic anhydride. The crude product was recrystallized three times from ethyl alcohol; m.p.: 78°.

3-*Nitrobenzyl phenyl sulphone:* 3-nitrobenzyl chloride and the sodium salt of benzene sulphinic acid were heated in alcoholic medium on a water bath. The sulphone obtained was recrystallized three times from glacial acetic acid;[27] m.p.: 163°.

4-*Nitrobenzyl phenyl sulphone:* was obtained by the reaction of 4-nitrobenzyl chloride with the sodium salt of benzene sulphinic acid;[27] the product was recrystallized three times; m.p.: 206–5°.

(3-*Nitrophenyl*) *phenylmethane:* was produced by the reaction of 3-nitrobenzyl chloride with benzene in the presence of aluminium chloride.[28] The product was then chromatographed on aluminium oxide. The oil was not distillable.

(4-*Nitrophenyl*) *phenylmethane:* was synthesized by the reaction of 4-nitrobenzyl alcohol and benzene in the presence of concentrated sulphuric acid.[28] Purification was performed by distillation *in vacuo*, followed by recrystallization from ligroin; m.p.: 30°, b.p.: 202°/11 torr.

3-*Nitrobenzenesulphonyl chloride:* was obtained by the action of chlorosulphonic acid on nitrobenzene.[29] The crude product was recrystallized three times from ether; m.p.: 63°.

4-Nitrobenzenesulphonyl chloride: was prepared from the sodium salt of 4-nitrobenzene sulphonic acid with phosphorus pentachloride.[30] The product was recrystallized three times from petroleum ether; m.p.: 76°.

(3-Nitrophenyl) phenyl sulphone: was synthesized by the action of 3-nitrobenzenesulphonyl chloride on benzene in the presence of aluminium chloride,[31] and recrystallized three times from ethyl alcohol; m.p.: 81°.

(4-Nitrophenyl) phenyl sulphone: 4-nitrobenzenesulphonyl chloride was reacted with benzene in the presence of aluminium chloride to yield the product[31] which was recrystallized three times from a mixture of alcohol and water; m.p.: 143°.

(3-Nitrophenyl) methyl sulphone: was obtained by the reaction of the silver salt of 3-nitrobenzene sulphinic acid with methyl iodide,[32] and recrystallized three times from distilled water; m.p.: 146°.

(4-Nitrophenyl) methyl sulphone: the silver salt of 4-nitrobenzene sulphinic acid was allowed to react with methyl iodide;[32] the product was recrystallized three times from alcohol; m.p.: 142·5°.

3-Nitrobenezenesulphonamide: was prepared by the reaction of 3-nitrobenzenesulphonyl chloride with aqueous ammonia.[29] The product was recrystallized four times from ethyl alcohol–water (1:1); m.p.: 167°.

4-Nitrobenezenesulphonamide: 4-nitrobenzenesulphonyl chloride was reacted with an aqueous solution of ammonia;[33] the product was recrystallized twice from ethyl alcohol–water; m.p.: 179–180°.

3-Nitrobenzenesulphonic acid ethyl ester: the reaction of 3-nitrobenzenesulphonyl chloride with sodium ethoxide afforded the product which was purified by distillation *in vacuo* and recrystallization from ether, m.p.: 36°.

4-Nitrobenzene sulphonic acid ethyl ester: was obtained by the reaction of 4-nitrobenzenesulphonyl chloride with sodium ethoxide; it was recrystallized four times from alcohol; m.p.: 90·5°.

3-Nitro-t-butylbenzene: was prepared from 3-nitro-4-amino-*t*-butyl-benzene by diazotization and subsequent reductive boiling.[34] The product was purified by distillation *in vacuo*; b.p.: 250–252°/704 torr.

4-Nitro-t-butylbenzene: was obtained from *tert.* butylbenzene with concentrated nitric acid at 0–5°.[35] The product was separated from the *ortho* compound by fractional crystallization and purified by distillation *in vacuo*; m.p.: 30°, b.p.: 274–275°/738 torr.

EXPERIMENTAL RESULTS

Figure 1 presents the conversion-time curves for various inhibitor concentrations (the inhibitor was: *m*-nitrobenzenesulphoamide).

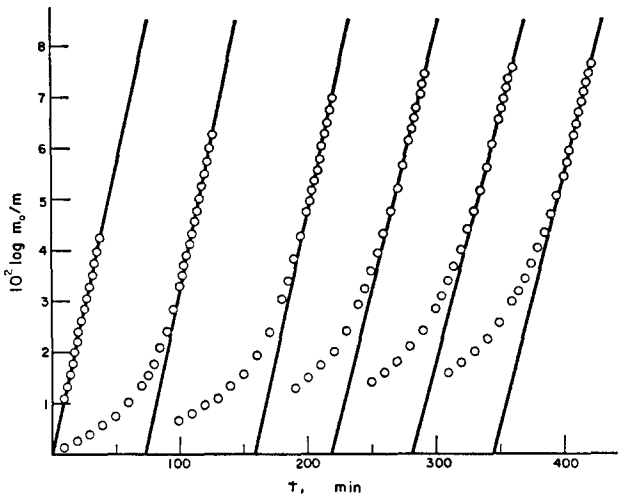


FIG. 1. Kinetic curves for the vinyl acetate/AIBN/*m*-nitrobenzenesulphonamide system at 50°.

TABLE 1. KINETIC DATA FOR SYSTEM VINYL ACETATE/AIBN/SUBSTITUTED NITROBENZENE, AT 50°

No.	Substituent	Initiator concentration $x_0 \times 10^3$ (mole/l.)	Inhibitor concentration $z_0 \times 10^5$ (mole/l.)	Length of inhibition period t_i (min)	Relative reactivity of inhibitor k_5/k_2
1		7·21	15·67	269	12·25
2		7·41	19·02	330	11·93
3		8·59	22·65	378	11·82
4	H	6·82	22·88	450	11·76
5		7·08	25·67	520	12·20
6		8·16	32·21	544	11·85
7		6·28	28·99	639	12·47
				$\mu = 1·66$	$12·04 \pm 0·27$
8		7·90	4·61	107	45·09
9		7·13	8·32	182	46·17
10	m-SO_2NH_2	7·51	12·04	262	44·92
11		7·78	15·87	337	43·25
12		7·79	19·30	413	39·71
13		7·52	21·92	488	43·22
				$\mu = 2·02$	$43·73 \pm 2·28$

TABLE 2. KINETIC DATA FOR THE SYSTEM VINYL ACETATE/AIBN/SUBSTITUTED NITROBENZENE, AT 50°

No.	Substituent	Number of exp.	Initiator concentration $x_0 \times 10^3$ (mole/l.)	Inhibitor concentration $z_0 \times 10^5$ (mole/l.)	Stoichiometric coefficient μ	Relative reactivity of inhibition k_5/k_2
1	p-CH_2Br	6	6·62– 9·62	3·09–20·55	2·23	$19·21 \pm 0·54$
2	m-CH_2Br	6	6·38– 9·24	3·70–17·59	1·99	$18·01 \pm 0·34$
3	p-CH_2Cl	6	7·24– 7·93	4·46–21·98	2·04	$17·67 \pm 0·56$
4	m-CH_2Cl	6	6·86– 8·29	4·95–28·33	2·23	$15·50 \pm 0·39$
5	p-CH_2CN	5	7·27– 8·56	5·62–20·69	1·88	$19·56 \pm 0·58$
6	m-CH_2CN	6	7·43– 8·71	5·23–25·91	2·12	$18·47 \pm 0·66$
7	p-CH_2NO_2	3	9·45–10·38	10·18–27·98	1·94	$24·77 \pm 0·59$
8	m-CH_2NO_2	3	9·70–10·68	11·03–28·81	2·22	$23·01 \pm 0·42$
9	p-$CH_2C_6H_5$	6	9·39–12·07	4·97–24·30	1·94	$10·34 \pm 0·55$
10	m-$CH_2C_6H_5$	3	8·29–10·30	14·10–28·03	2·03	$10·55 \pm 0·55$
11	p-$CH_2SO_2C_6H_5$	6	9·14–12·60	4·04–21·39	2·54	$18·50 \pm 0·41$
12	m-$CH_2SO_2C_6H_5$	6	8·49–12·41	4·05–16·96	2·48	$17·91 \pm 0·55$
13	p-$C(CH_3)_3$	6	7·37– 7·94	4·70–24·71	1·89	$9·51 \pm 0·18$
14	m-$C(CH_3)_3$	6	9·58–10·71	5·88–26·30	1·50	$10·03 \pm 0·19$
15	p-CH_2OCOCH_3	3	9·96–11·37	11·67–20·33	2·53	$15·17 \pm 1·25$
16	m-CH_2OCOCH_3	3	10·12–12·21	10·70–24·97	2·62	$14·61 \pm 0·92$
17	p-SO_2NH_2	6	7·42– 7·86	4·18–20·68	1·94	$50·61 \pm 0·78$
18	p-SO_2Cl	6	7·34– 8·97	5·63–19·56	1·83	$165·30 \pm 2·47$
19	m-SO_2Cl	6	7·19– 8·25	3·69–17·17	1·88	$110·90 \pm 1·46$
20	p-SO_2CH_3	5	8·21–10·35	10·72–23·95	1·96	$65·91 \pm 1·65$
21	m-SO_2-CH_3	6	8·26– 8·95	4·96–24·90	1·83	$53·51 \pm 1·38$
22	p-$SO_2C_6H_5$	6	6·19– 8·50	3·46–14·87	1·81	$70·18 \pm 1·36$
23	m-$SO_2C_6H_5$	6	7·16– 8·70	3·43–18·88	1·90	$54·72 \pm 0·47$
24	p-$SO_2OC_2H_5$	3	9·68–11·74	10·00–16·80	1·92	$74·97 \pm 0·37$
25	m-$SO_2OC_2H_5$	3	9·36–11·73	8·08–18·14	1·85	$55·94 \pm 0·77$

It can be seen that this compound exerts a regular inhibition effect on the polymerization of vinyl acetate: during the period of inhibition, the reaction rate gradually increases, and, when the inhibitor is exhausted, the stationary rate corresponds to the rate of the uninhibited polymerization of vinyl acetate. Similar kinetic curves were obtained for the other nitro compounds studied. The results of kinetic measurements could be very well interpreted according to ideas of simple inhibition.[36,20] The kinetic parameters are collected in Tables 1 and 2.

It could be observed that, for all nitro compounds under investigation, the length of the inhibition period is a strictly linear function of the inhibitor concentration. A characteristic example is shown in Fig. 2. (cf. Table 1).

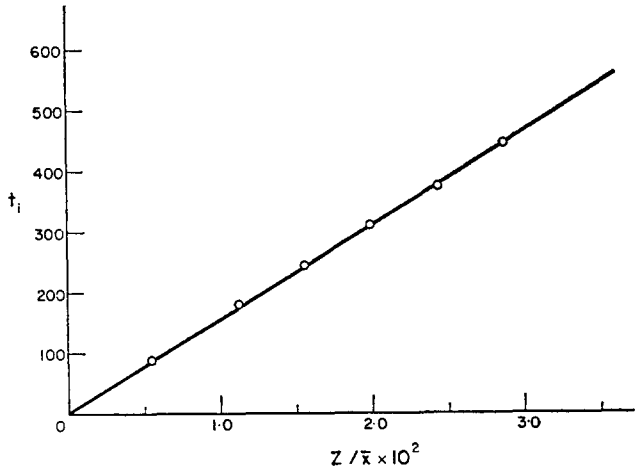
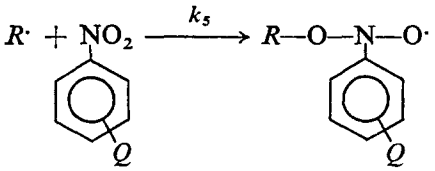


FIG. 2. Dependence of the inhibition period on the concentration of the inhibitor in the case of vinyl acetate/AIBN/*m*-nitrobenzenesulphonamide at 50°.

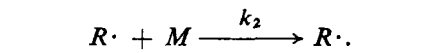
The strict linearity of this relationship clearly indicates that, besides the simple inhibition, there are no side reactions in the systems investigated.[37] The stoichiometric coefficient values (μ) for the individual inhibitors are also indicated in Tables 1 and 2; the values range between 1·6 and 2·5. Interpretation of these results, based on the hot radical hypothesis,[49] will be dealt with in a later publication.

The reactivities of substituted nitro compounds relative to vinyl acetate can be accurately determined from the kinetic data (k_5/k_2),[20] where k_5 stands for the rate constant of the inhibition reaction:



(3)

and k_2 denotes the rate constant of the chain propagation reaction:



(4)

The average values of k_5/k_2 as well as the root mean square errors are listed in Tables 1 and 2.

The average values of relative reactivity (k_5/k_2) and the logarithms of the reactivities relative to nitrobenzene are shown in Table 3. The designations used in the table and subsequently are:

k_5/k_2 (nitrobenzene) $= k^0$
k_5/k_2 (*para*-substituted nitrobenzene) $= k_p$
k_5/k_2 (*meta*-substituted nitrobenzene) $= k_m$.

TABLE 3

No.	Substituent	k_p $(k_5/k_2)_p$	log k_p/k^0	k_m $(k_5/k_2)_m$	log k_m/k^0	σ_I
1	—H	12·04	0			0
2	—$CH_2C_6H_5$	10·34	−0·066	10·55	−0·058	−0·08 (16)
3	—$C(CH_3)_3$	9·51	−0·101	10·03	−0·079	−0·07 (10)
4	—CH_2NO_2	24·77	0·313	23·01	0·283	—
5	—CH_2CN	19·56	0·211	18·47	0·186	0·16 (16)
6	—CH_2Cl	17·67	0·167	15·50	0·110	0·11 (16)
7	—CH_2Br	19·21	0·203	18·01	0·175	—
8	—$CH_2SO_2C_6H_5$	18·50	0·187	17·91	0·173	0·15 (16)
9	—CH_2OCOCH_3	15·17	0·100	14·61	0·084	—
10	—SO_2NH_2	50·61	0·624	43·73	0·560	0·53 (16)
11	—SO_2CH_3	65·91	0·738	53·51	0·648	0·64 (16)
12	—$SO_2C_6H_5$	70·18	0·766	54·72	0·658	0·62 (16)
13	—SO_2Cl	165·30	1·138	110·90	0·964	—
14	—$SO_2OC_2H_5$	74·97	0·794	55·94	0·668	0·63 (42)

DISCUSSION

If the *para*- or *meta*-substituents of the aromatic ring exert only an inductive effect on the rate constant of a reaction, then, on the basis of the Hammett equation and Eqns. (1) and (2), as well as conclusions drawn from the literature,[38,16] the following linear relationship must be valid:

$$\log k_p/k^0 = \lambda \log k_m/k^0. \tag{5}$$

The relative reactivity values derived by us are illustrated by Eqn. (5) in Fig. 3. The linear relationship obtained suggests that the —CH_2X and —SO_2X substituents under investigation affect the reactivity of the nitro group according to the same mechanism.

The question arizes whether this effect can be associated exclusively with the inductive effect of the substituent. In the case of —CH_2X and —SO_2X type substituents, the occurrence of hyperconjugation or conjugation is also assumed.[39,40]

A number of references[41] contradict the possibility of hyperconjugation in the case of —CH_2X substituents. According to the investigations, the rate constants or dissociation constants for different reactions carried out with benzene derivatives containing such substituents show linear correlation with the inductive constants of these substituents. (Only in the case of the —CH_3 group can some slight deviation be observed, occasionally.) Notably, unlike other substituent constants, the inductive constants determined by different methods give a common scale and are independent of the nature of the reaction used for the determination.[42]

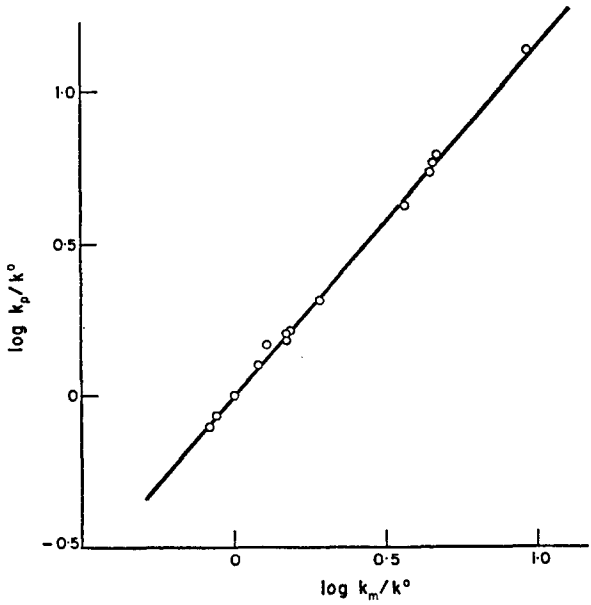


FIG. 3. Reactivity of *para*- and *meta*- substituted nitrobenzenes plotted according to Eqn. (5).

With $-SO_2X$ type substituents, the following factors suggest the lack of conjugation. The linear relationship[5] may be valid even if the substituents have a mesomeric effect but only when $\alpha\lambda = 1$.

The results of further investigations, to be dealt with in our next communication,* show that the mesomeric effect exerted by all other substituents (e.g. $-COX$, $-NHX$, —OH, —F, —Cl, —Br, etc.) is four times as great for the *para* position as for the *meta* position, so excluding the possibility of $\alpha\lambda$ being unity. On the other hand, if in addition to the inductive effect, the substituent exerts a mesomeric effect on the rate constant, this effect must be reflected in deviation from the linear relationship $\log k/k^0 = f(\sigma_I)$. The dependence of reactivity values on the σ_I constants (see Table 3) is indicated in Fig. 4. It is evident that this relationship is linear within experimental error.

Thus, the conclusion can be drawn that in the particular radical reaction, $-CH_2X$ and $-SO_2X$ type substituents have an exclusively inductive effect on the reactivity of the nitro group. As can be seen in Figs. 3 and 4, the inductive effect of the substituent is much more intensive when it is in the *para* position than when it is in the *meta* position; by the method of least square, we find $\lambda = 1{\cdot}15$.

In the literature, several sets of data refer to the λ value. A study of the individual model systems revealed that in certain cases λ was less than 1[14,43,44] and in other cases it was larger than 1.[15,16,42,45,46] The value of λ was, however, in some cases calculated from data referring to only one substituent.[43,46] The most reliable and extensive experimental data are due to Exner *et al.*[15,16,47] These authors studied the effects of a number of substituents, both in the *para* and the *meta* positions, on the dissociation constants of benzoic acids; by analysis of the σ values, they showed that

* The kinetics of radical polymerization, XXVI.

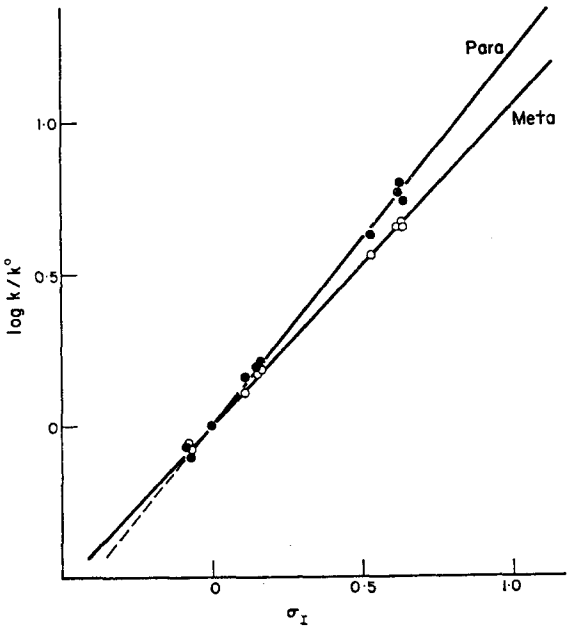


FIG. 4. Dependence of the reactivity of substituted nitrobenzenes on inductive constants (σ_I).

many substituents (e.g. $—CH_2X$, $—SO_2X$, $—NO_2$, —CN) do not enter into conjugation with the benzene ring. For the value of λ, they obtained 1·14 and verified that this value is independent of the solvent. In interpreting the numerical value $\lambda > 1$, they assumed that in addition to σ-bonds, also π-electrons participate in the transfer of the *I*-effect (the so-called non-classical I_π effect[13,48]).

Comparing our results and those obtained by Exner and considering the fact that two entirely different types of reaction are involved, we may state that λ may be regarded as a constant entirely independent of the nature of the reaction.

By application of the values of λ, $\log k/k^0$ and σ_I, we found the ρ constant, characteristic of the reaction studied, to be +1·05.

Acknowledgement—Thanks are due to Mrs. B. Mohos for technical assistance.

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Résumé—On a étudié l'effet de quelques nitrobenzènes substitués en positions *para* et *méta* sur la polymérisation radicalaire de l'acétate de vinyle. On a montré que les substituants du type $—CH_2X$ et $—SO_2X$ ont simplement un effet inducteur sur la réactivité des groupements nitro. On a également établi que l'effet inducteur des substituants en position *para* est plus intense que celui des substituants en position *méta* c'est-à-dire $\lambda = 1{,}15$. On a trouvé que la constante ρ caractéristique de la réaction entre les radicaux poly(acétate de vinyle) et les nitro-benzènes substitués est égale à $+1{,}05$.

Sommario—Si è eseguito uno studio sull'effetto che alcuni nitrobenzeni *para-* e *meta*-sostituiti esercitano sulla polimerizzazione di acetato di vinile. Si è mostrato che i sostituenti di tipo $—CH_2X$ e $—SO_2X$ posseggono puramente un effetto induttivo sulla reattività dei gruppi nitro. Si è pure stabilito che l'effetto induttivo dei sostituenti è più intensivo quando essi sono in posizione *para* che invece in posizione *meta*, cioè con $\lambda = 1{,}15$.

Si è trovato che la costante ρ, caratteristica della reazione tra radicali di poli(vinil acetato) e nitrobenzeni sostituiti, è pari a $+1{,}05$.

Zusammenfassung—Der Einfluß von einigen *para* und *meta* substituierten Nitrobenzolen auf die radikalische Polymerisation von Vinylacetat wurde untersucht. Es wurde gezeigt, daß $—CH_2X$ und $—SO_2X$ artige Substituenten lediglich einen induktiven Effekt auf die Reaktivität der Nitrogruppen ausüben. Es wurde außerdem festgestellt, daß der induktive Effekt der Substituenten in *para* Stellung intensiver ist als in *meta* Stellung, d.h. $\lambda = 1{,}15$.

Die für die Reaktion zwischen den Polyvinylacetatradikalen und den substituierten Nitrobenzolen charakteristische Konstante ρ wurde zu $+1{,}05$ bestimmt.