

For identical polar heads the effectiveness should solely depend upon the hydrocarbon chain (this can be either a side chain or one having the polar head). Hence the following orders of effectiveness are justified: CPB > TDPB > LPB; CPC > LPC; Maroxol-OT > Manoxol-IB.

Molecules of a suppressor with a smaller polar head will crowd the double layer and its vicinity more and hence will be more effective, as in the case of CTAB and CDBAC.

Non-ionic or amphoteric substances suppress maxima on the basis of preferential adsorption on the mercury drop. The efficiency of these suppressors depends upon the potential range of the maxima. Different non-ionic suppressors are adsorbed on the mercury drop to different extents at a given potential. The order of effectiveness amongst the suppressors used is: Triton X-100 > Decon-90 > Amido black > ethyl diagol > 2-ethoxy ethanol.

Thanks are due to Dr O. P. Bansal and Dr S. N. Srivastava for their keen interest in this work and to Dr S. N. Dubey, Principal, Agra College, Agra, for providing necessary facilities.

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Kinetics of Reaction Between Substituted Benzoyl Chlorides & Anilines in Benzene

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Received 9 January 1976; accepted 8 July 1976

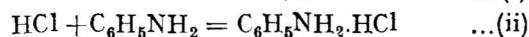
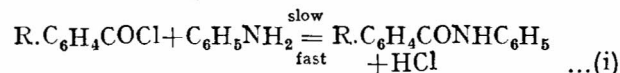
The resultant effect on the activation energy of two or three substituents in the benzene nucleus is nearly the sum of their individual effects. The reaction is bimolecular and the plot of specific rate constants against the dipole moments of substituted benzoyl chlorides is linear. The Hammett's equation is also applicable in the present case.

THE reaction of some mono substituted benzoyl chlorides and anilines in CCl_4 and hexane was studied by Grant and Hinshelwood¹ and in benzene

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by Williams and Hinshelwood and coworkers²⁻⁴. In this note we report the kinetics of reaction between di- and tri-substituted benzoyl chlorides with aniline in benzene. The conclusions drawn from the present study are similar to those reported by Saksena and Bose⁵.

Aniline reacts with substituted benzoyl chlorides as shown in Eqs. (i) and (ii).



Step (i) is the rate determining step. In order to study the reaction kinetics, standard solutions of aniline (0.04M) and substituted benzoyl chlorides (0.02M) were prepared in benzene. After equilibrating at the desired temperature ($30^\circ \pm 0.1^\circ$) the solution of benzoyl chloride (5 ml) was mixed with the solution of aniline (5 ml) in a reaction vessel containing benzene (10 ml), and the reaction mixture shaken well. The final concentrations of benzoyl chloride and aniline in the reaction mixture were 0.01M and 0.005M respectively.

The precipitate of aniline hydrochloride formed after definite intervals of time was filtered off through Gooch crucible. The reaction vessel was washed twice with benzene and finally with distilled water. To the washings and the precipitate was added 5 ml of 6N nitric acid to dissolve the precipitate completely. The chloride was estimated by Volhard's method.

A slightly modified bimolecular velocity constant equation was used for calculating k values for this reaction. If a is the initial concentration of substituted benzoyl chloride, $2a$ that of aniline and if x is the amount of substituted benzoyl chloride which reacted in time t , then the concentration of aniline that reacted should be $2x$.

Thus $dx/dt = k(a-x)(2a-2x)$, whence

$$k = \frac{1}{120t} \left(\frac{1}{100-Z} - \frac{1}{100} \right) \frac{100}{a}$$

where k is the velocity constant in litre mole⁻¹ sec⁻¹, t is the time in min and Z is the percentage conversion. The bimolecular rate constants have been found to be constant up to 70% conversion. The energy of activation was calculated by 'least square method' and also from the Arrhenius plot.

It is evident from the data given in Table 1 that there is marked variation of the energy of activation with the substituent. The energy of activation

TABLE 1 — ENERGY OF ACTIVATION AND FREQUENCY FACTOR AT 30° IN BENZENE

Benzoyl chloride	log A litre mole ⁻¹ sec ⁻¹	ΔE^\ddagger	$\log_{10} (R_{30}/\sqrt{M \times 10^6})$
—	4.41	—	1.8190
2,4-Dichloro-	4.11	+210	2.6224
3,5-Dinitro-	4.25	-530	2.6870
3-Nitro-4-chloro-	4.19	+60	2.6492
3,4-Dimethoxy-	4.61	+360	1.5699
3,4,5-Trimethoxy-	4.42	+100	1.5650
3-Methoxy-4-ethoxy-	4.48	—	1.3406

TABLE 2 — CONTRIBUTION OF THE SUBSTITUENT IN BENZOYL CHLORIDE AND ANILINE TO THE ACTIVATION ENERGY

Substituent group	ΔE^\ddagger (cal mole ⁻¹)	
	Benzoyl chloride	Aniline
<i>o</i> -Chloro-	-900	+2980
<i>p</i> -Chloro-	-400	+930
<i>m</i> -Nitro-	-960	+3040
<i>p</i> -Nitro-	-1700	+4430
<i>m</i> -Bromo-	-740	+1740
<i>m</i> -Methoxy-	-200	—
<i>p</i> -Methoxy-	+900	—

when plotted against $\log k_{20}$ gives a linear plot with the slope $\approx 2.303 RT$, indicating that for these compounds the entropy of activation is constant. The variations in the velocity constant at a given temperature caused by different substituents in benzoyl chloride are due to the changes in the energy of activation.

The energy of activation of benzoyl chloride being 7600 cal g⁻¹ mole⁻¹, the changes in activation energy (ΔE^\ddagger) caused by various substituents present in substituted benzoyl chlorides have been calculated and the results obtained are given in Table 2. The theoretical values for the activation energies of di- and tri-substituted benzoyl chlorides have been calculated by the addition of the value of ΔE for the substituent groups to the value of activation energy of benzoyl chloride. The value of 2,4-dichlorobenzoyl chloride and 3,4,5-trimethoxy benzoyl chloride have been calculated in the following manner:

(i) Energy of activation of 2,4-dichlorobenzoyl chloride $7600-900-400 = 6300$ cal g⁻¹ mole⁻¹ (experimental value = 6900 cal⁻¹ mole⁻¹) and (ii) energy of activation of 3,4,5-trimethoxybenzoyl chloride $7600-200+900-200 = 8100$ cal g⁻¹ mole⁻¹ (experimental value = 8000 cal g⁻¹ mole⁻¹).

Thus experimental values of energy of activation of di- and tri-substituted benzoyl chlorides are in good agreement with the calculated values. It is interesting to compare the effect of substituents in aniline and in benzoyl chloride on the reaction rate. It is observed (Table 2) that *ortho*-chloro group in the benzoyl chloride decreases the energy of activation, whereas the *o*-chloro group in aniline increases the energy of activation. In the case of *para*-methoxybenzoyl chloride the energy of activation is increased by 900 cal mole⁻¹. As the methoxy group increases the quinonoid structure in both the initial and transitional state of benzoyl chloride, it will therefore increase the activation energy, which has actually been observed.

The plot of dipole moments of substituted benzoyl chlorides versus energies of activation is linear in conformity with the observations of Nathan and Watson⁶ and Grant and Hinshelwood⁷.

This reaction studied also fits well with Hammett's equation⁸. The positive slope value (+1.406) for the Hammett plot indicates that the reaction is aided by the electron withdrawing group in benzoyl chloride.

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Some Novel Di- & Tetra-cyclopentadienyltungsten(VI) & Di- & Tetra-indenyltungsten(VI) Oxides & Sulphides

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Received 26 May 1976; accepted 24 July 1976

Some new di- and tetra-cyclopentadienyltungsten(VI) and di- and tetra-indenyltungsten(VI) oxides and sulphides have been prepared and characterized on the basis of analytical and IR data. Structures with σ - and π -bonded rings, which are not in the same plane, are proposed.

DICYCLOPENTADIENYL- and diindenyltungsten(VI) oxydichlorides¹ and their pseudohalide derivatives² have been reported in literature. Tetracyclopentadienyl- and tetraindenyltungsten(VI) oxides³ are also mentioned in the literature, but there is no reference about the preparation and characterization of the di- and tetra-cyclopentadienyl- and indenyltungsten(VI) sulphides and oxides. This note describes the preparation and characterization of these compounds.

All the reactions were carried out in dry atmosphere. Tetrahydrofuran was purified and dried before use by distillation over lithium aluminium hydride. Freshly distilled cyclopentadiene and indene were used as such or for the preparation of their sodium salts. Tungsten was estimated as WO₃, carbon and hydrogen were estimated by microanalytical methods and sulphur was estimated as BaSO₄. Infrared spectra were recorded on a Perkin-Elmer spectrophotometer model-137 in KBr.

WS₃ (chocolate colour) was prepared by passing H₂S through ammonium tungstate solution and acidifying the resulting yellow thiotungstate solution. WS₂Cl₂, (C₅H₅)₂WOCl₂ and (C₉H₇)₂WOCl₂ were prepared as described in literature^{4,5}. WO₂Cl₂ (yellow crystals) was prepared by exposing the scarlet red crystals of WOCl₄ to dry atmosphere till they turned yellow and then purified by sublimation.

Tetracyclopentadienyltungsten(IV) sulphide — To a suspension of WS₃ (1.12 g, 0.004 mole) in tetrahydrofuran (100 ml) were added freshly distilled cyclopentadiene (1.2 ml, 0.017 mole) and diethyl-

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