On the Correlation between the Carbonyl Vibrational Frequency of Substituted Thenoyl Chlorides and the Rate of their Reaction with Aniline

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An interpretation is proposed for the observed linear correlation between the carbonyl i.r. of 3- and 5-substituted thenoyl chlorides and the logarithm of the rate constant of their reaction with aniline. Simple Hückel MO theory, both in its complete form and in its perturbation approximation, shows that the substituent effect on the π-electron population of the carbon atom of the C=O group is linearly related to the substituent effect on the reaction rate. The activation energy of the reaction has been evaluated from the HMOs of the separate molecules by fitting them into a supermolecule scheme. The bond formed in the activated state was treated as a charge transfer from the HOMO of aniline to the LEMO of the substituted thenoyl chlorides. This model accounts for the observed correlation between the substituent effect on the reaction rate and that on the ν(C=O) absorption band. The complete HMO treatment gives a better agreement than the perturbation approach. The following suggestions are made. (i) A similar correlation is expected for the substituent effect in furan- and pyrrole-2-carbonyl chlorides. (ii) A search should be made for a charge-transfer absorption band in the spectra of the reacting molecules.

VARIOUS examples of correlations between ν(C=O) and reaction rates have been reported in the literature.[1] This is an interesting result, and means that the same combination of factors is responsible for both a shift in the carbonyl stretching frequency and a change in the reaction rate. The theoretical interpretation however is not immediately obvious, since ν(C=O) is a ground state property of the isolated molecule and log$k$ is instead a dynamic quantity dependent on the structure of the reacting system as represented by the so-called activated complex. The uncertainty in the actual structure, the size of the reacting molecules, and the role of solvent effects prevent a general study of the correlation by accurate MO SCF procedures.

Arcoria and his co-workers [2] have recently found that the same correlation holds for the substituent effect in the reaction of **3**- and **5**-substituted **2**-thenoyl chlorides with aniline (Figure 1). This makes it a somewhat easier problem, and the nearly constant activation entropy allows discussion in much simpler terms. The results reported here show that a fair measure of understanding can be obtained by a judicious use of the Hückel approximation.

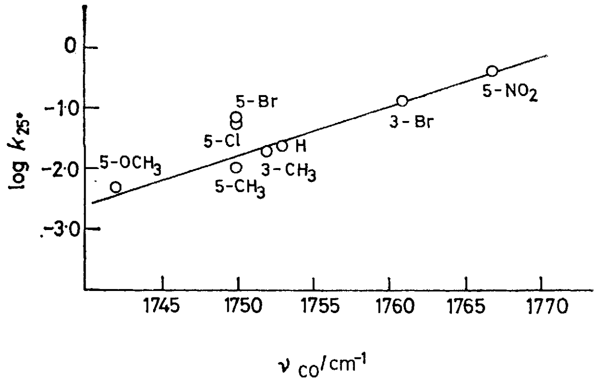
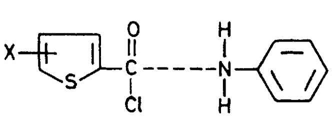


FIGURE 1 Linear correlation between the rate of reaction (log$k$) of aniline with substituted thenoyl chlorides, and the C=O stretching frequency of the latter compounds (plot from data of ref. 2)

METHODS AND RESULTS

The Isolated Molecules.—The most likely structure (A) for the transition state involves an attack of the lone pair of the amino-group on the carbonyl carbon atom.



(A)

Two different approximations have been used for studying the effect of the substituent on the thiophen ring of thenoyl chloride. (i) The substituent X is taken into account by adding a $2p\pi$ atomic orbital and an electron pair to the system, through an appropriate choice of parameters. After a literature survey [3] and some preliminary calculations, a set of parameters h_i for the coulomb integrals and k_{ij} for the resonance integrals of the involved molecules was adopted ($\alpha_i = \alpha + h_i\beta$, $\beta_{ij} = k_{ij}\beta$) (Table). (ii) The substituent effect is reduced to a perturbation localized on the ring carbon atom, $\alpha_i = \alpha + \delta\beta$ (i = 3 or 5), where δ is varied within a certain range.

Atom	h_i	Bond	k_{ij}
C	0	C–S	1
O	2	C(2)–C(3), C(4)–C(5)	1.09
Cl	2	C(3)–C(4)	1
S	1.5	C–CO	0.87
X	1 or 2	C–Cl	0.4
N	0.5	C=O	1.65
		C–X	0.3—1.6
		C–N	0.5

The vibrational frequency of the carbonyl group was obtained through a relationship established previously [4] and able to reproduce the correlation between the ν(CO) frequency and the $\Delta\nu$(XH) shift in hydrogen-bonded associations [equation (1)]. Here p is the CO π bond order as

$$\nu(\mathrm{CO}) = A(5 + 9p)^{\frac{1}{2}} \tag{1}$$

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[1] (a) R. N. Jones, W. F. Forbes, and W. A. Mueller, *Canad. J. Chem.*, 1957, **35**, 504; (b) H. A. Staab, W. Otting, and A. Ueberle, *Z. Elektrochem.*, 1957, **61**, 1000; (c) R. Stewart and K. Yates, *J. Amer. Chem. Soc.*, 1958, **80**, 6355; (d) A. Arcoria, S. Fisichella, G. Scarlata, and D. Sciotto, *J. Org. Chem.*, 1974, **39**, 3025 and references therein.

[2] A. Arcoria, personal communication; G. Alberghina and S. Fisichella, *Chimica e Industria*, 1976, **58**, 380.

[3] A. Streitwieser, 'Molecular Orbital Theory,' Wiley, New York, 1961, chs. **4** and 5.

[4] L. Paoloni, A. Patti, and F. Mangano, *J. Mol. Structure*, 1975, **27**, 123.

defined by Coulson, and A a constant whose value depends on the choice of a suitable reference compound, $COCl_2$ in the present case. Its vapour phase carbonyl stretching frequency [5] is 1 827 cm^{-1}, and corresponds to a Urey–Bradley force constant [6] of 12.61 mdyn $Å^{-1}$. From these data the value of A is 514.5.

The parametrization of the β_{CO} integral was found to be most influential in determining the C=O bond order and therefore in placing the ν(CO) frequency within the experimental range 1 740—1 770 cm^{-1}. A choice of $\beta_{CO} = 1.53\beta$ gives the experimental ν(CO) = 1 753 cm^{-1} of unsubstituted thenoyl chloride, but does not allow the complete calculations (i) to extend over the same range covered by the perturbation treatment (ii). Since our study is concerned with the general pattern of the experimental correlation (and not in playing with the parameters until a perfect numerical fit is found) we fixed $\beta_{CO} = 1.65\beta$ to reproduce the same experimental ν(CO) range for both calculations (i) and (ii). A continuous variation of δ within less than 2 β-units is sufficient to cover the ν(CO) experimental range. Since the corresponding variations in the total π-electron energy are 5—7%, we consider the perturbation treatment justified. With these choices the frequency goes from the upper to the lower limit when k_{CX} is varied stepwise from 0.3 to 1.6 or when δ is varied from 0 to -1.4.

In both cases a linear relation is found between the π-electron vacancy (net charge) on the carbon atom of the carbonyl group and the ν(CO) frequency calculated from equation (1). As shown in Figure 2 the slope is the same whatever approximation is adopted and independent of the substituent position, 3 or 5, in the ring.

The Model for the Activated Complex.—The π-electron vacancy of the carbonyl group seems to be the main factor which controls the dependence of the reaction rate on the substituent. Its partner must be the electronic population of the aniline nitrogen atom, and the process of establishing the new C–N bond can be considered to occur through a σ-charge-transfer process. In terms of the Hückel MO approach we considered this to correspond to the transfer of one electron from the highest occupied MO (HOMO) of aniline to the lowest empty MO (LEMO) of thenoyl chloride.

A simple and convenient method for building up this activated complex ' supermolecule ' seemed to us to be the well known procedure proposed by Mulliken for charge-transfer molecular complexes.[7] The complex wave function is $\Phi = a\psi_0(D,A) + b\psi_1(D^+A^-)$, where $\psi_0(D,A)$ is the no-bond structure function of aniline (D) and thenoyl chloride (A), and $\psi_1(D^+A^-)$ the dative structure function of the molecular complex. We used the molecular orbital functions of the isolated species, and their respective eigenvalues, for obtaining the diagonal terms of the energy matrix solution of the variational problem.[7b] The out-of-diagonal term H_{01} was evaluated with the following approximations. (i) The antisymmetrization of the ψ_0 and ψ_1 functions was limited to the pair of electrons involved in the bonding interaction. (ii) The corresponding hamiltonian was written as $H(1,2) = h(1) + h(2) + (1/r_{12})$. (iii) The overlap integral between the HOMO of aniline and the LEMO of thenoyl is taken equal to the overlap integral S_{CN} between the $2p\pi$ atomic orbitals of the aniline nitrogen and of the thenoyl carbonyl carbon, mutually oriented along the same axis of bonding approach.

Within this framework the H_{01} integral is given by equation (2) where ε_{HOMO} is the eigenvalue of the aniline HOMO, c_N and c_C the $2p\pi$ atomic orbital eigenvectors in the HOMO and LEMO of the respective molecules, R the nitrogen–carbon contact distance, and $\beta^*_{CN} = \langle\phi_{HOMO}|h(1)|\phi_{LEMO}\rangle \simeq S_{CN}\beta$.

$$H_{01} = 2^{\frac{1}{2}}(S_{CN}\varepsilon_{HOMO} + \beta^*_{CN} + c_N{}^3\, c_C S_{CN}/R) \qquad (2)$$

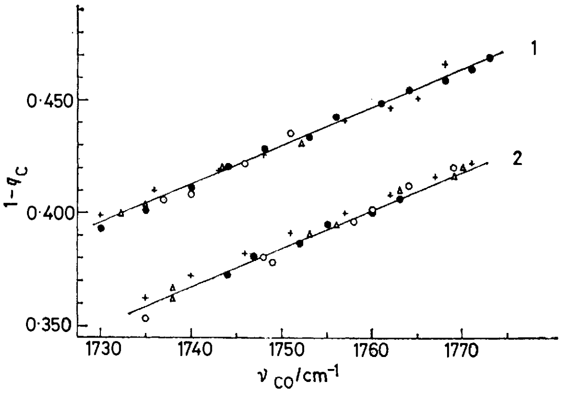

FIGURE 2 Plot of the calculated net charge in the π-orbital of carbon *versus* the stretching frequency of the C=O group predicted from the π-bond order. Line 1 corresponds to $k_{CO} = 1.53$ and line 2 to $k_{CO} = 1.65$ (see text). The two points at 1 638 cm^{-1} on line 2, obtained for complete calculations on a methoxy-like substituted compound refer to different parametric choices: the lower to $h_X = 2$ and $k_{CX} = 1.2$ and the upper to $h_X = 1$ and $k_{CX} = 1.6$. +, 3-substituted perturbation; ●, 5-substituted, perturbation; △, 3-substituted, complete; ○, 5-substituted, complete

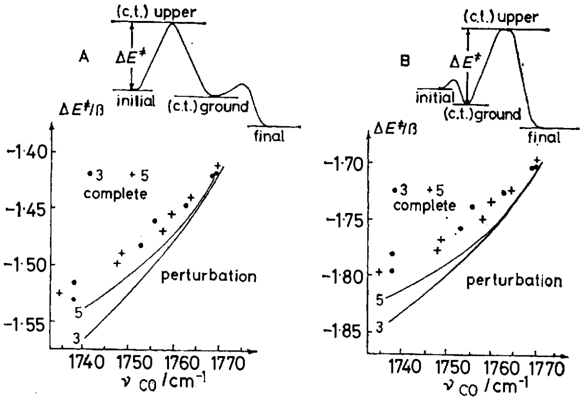

FIGURE 3 Calculated correlation between the activation energy of the reaction of aniline with substituted thenoyl chlorides and the C=O stretching frequency of the latter compounds. A is calculated from equation (4) and B from equation (3)

After diagonalization of the 2 × 2 energy matrix a choice has to be made in order to calculate the activation energy of the reaction. This depends on whether one considers the ground state of the complex as being formed before or after the activated state, which corresponds to the upper state of the molecular complex. In the first case the activation

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[5] J. Overend and J. C. Evans, *Trans. Faraday Soc.*, 1959, **55**, 1817.

[6] J. Overend and J. R. Scherer, *J. Chem. Phys.*, 1960, **32**, 1296.

[7] (*a*) R. S. Mulliken and W. B. Person, ' Molecular Complexes,' Wiley, New York, 1969, pp. 9—13, 374—380; (*b*) R. D. Brown, *J. Chem. Soc.*, 1959, 2224, 2232.

energy is given by equation (3) and in the alternative by equation (4).

$$\Delta E^{\ddagger} = [(\varepsilon_{\mathrm{HOMO}} - \varepsilon_{\mathrm{LEMO}})^2 + 4H_{01}{}^2]^{\frac{1}{2}} \tag{3}$$

$$\Delta E^{\ddagger} = \tfrac{1}{2}(\varepsilon_{\mathrm{LEMO}} - \varepsilon_{\mathrm{HOMO}}) + \tfrac{1}{2}[(\varepsilon_{\mathrm{HOMO}} - \varepsilon_{\mathrm{LEMO}})^2 + 4H_{01}{}^2]^{\frac{1}{2}} \tag{4}$$

We assumed an interaction distance R of 2 Å and adopted for β the literature[8] value of -3.14 eV. The results are presented in Figure 3. The perturbation treatment seems less adequate because it tends to distinguish the 3- from the 5-substituted isomers at least on the lower side of the ν(CO) frequencies. The points calculated from the complete treatment are fairly aligned and therefore can account for the experimental relationship at least in qualitative terms.

DISCUSSION

Our treatment is apparently successful on two main points which are the underlying assumptions in various papers:[1,2] the correlation of the vibrational frequency of the C=O group with the π-electron density on the carbon atom and the leading role of this parameter in the reactions of the molecule. There are, of course, a number of limitations, which we discuss. A crucial point is equation (1): as already pointed out[4] its confidence level is the same as that of the observed correlation between bond order and bond length. The model does not require a definite interaction geometry except for the $H_2N \cdots C{=}O$ distance, fixed at 2 Å, somewhat shorter than the sum of the Kitaigorodsky intermolecular radii[9] for nitrogen and carbon, which is *ca.* 3.4 Å. The calculated activation energy, approximately proportional to the overlap integral S_{CN}, would be smaller at a larger distance. An accurate prediction of its value is however well beyond the scope of the Hückel method.

The procedure used to calculate the activation energy, based on the formalism of the charge-transfer model, does not imply that a charge-transfer complex is formed between aniline and the thenoyl chlorides, although we consider its formation a definite possibility. The reaction between substituted anilines and chloranil has been shown by Nagakura and his co-workers[10] to start by the formation of an outer π-complex: a fading absorption band appears when solutions of aniline and chloranil are mixed. There is no report of a similar finding in the reaction of aniline, or its derivatives, with benzoyl, furoyl, or thenoyl chlorides. We suggest a search for a transient colour, possibly with suitably substituted reagent molecules.

When h_{S} and k_{CS} of thiophen are varied over a relatively wide range ν(CO) changes only slightly. Since such a parametric change is equivalent to a substitution of the sulphur atom with oxygen or nitrogen, our calculations predict that a correlation like that of Figure 1 is to be expected in the reaction of aniline with substituted furan- and pyrrole-2-carbonyl chlorides.

Finally we make a tentative suggestion for the anomalous position of 5-chloro- and 5-bromo-thenoyl chlorides in Figure 1: the geometry of the activated complex may favour a charge-transfer interaction between the reacting molecules. The chlorine or bromine substituent acting as electron acceptor for the aniline π-electron system, would reduce the activation energy and shift the reaction rate to a higher value than determined by the π-electron density of the carbonyl carbon atom.

We are grateful to Professor Arcoria and his colleagues for making available their unpublished results, and for helpful discussions and comments.

[7/514 *Received*, 23*rd March*, 1977]

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[9] A. I. Kitaigorodsky, 'Molecular Crystals and Molecules,' Academic Press, New York, 1973, p. 10.

[10] (*a*) T. Nogami, K. Yoshihara, H. Hosoya, and S. Nagakura, *J. Phys. Chem.*, 1969, **73**, 2670; (*b*) T. Nogami, K. Yoshihara, and S. Nagakura, *Bull. Chem. Soc. Japan*, 1972, **45**, 122.