

by a positively charged reagent according to (1) brings towards the position of attack the π -electron pair occupying the most tightly bound energy level. Simultaneously all other pairs are progressively removed from this region. The physical implications of (1) are therefore inconsistent with bond formation by the frontier electrons.

In the same way nucleophilic attack, represented by $\delta\alpha$, positive in (1) produces a reduced amplitude of the frontier electrons at the region of attack, a result incompatible with the frontier-orbital hypothesis.

Of the two theories which correlate equally well with experimental data, the frontier-orbital concept is more readily acceptable by comparison with conventional bonding by the least-bound electrons of the reacting systems. Nevertheless polarization of the π -electron system by the ionic reagent itself precludes this hypothesis by reason of the physical- and quantum-mechanical principles controlling the charge shifts.⁵

The frontier orbitals appear to be significant in the case of free-radical attack. The charge-distribution method associates the ease of radical attack with the free valence F , at an atom⁶ which may be related to the change in π -electron energy due to a change in resonance integral of the bonds adjacent to the position of attack. The corresponding change in π -electron configuration results in a reduction in amplitude at the position of attack of all MO's except the frontier orbitals. These are not, however, distorted towards the region of attack, but remain distributed throughout the conjugated system, and tend to form a degenerate pair of zero-binding energy. A suitable linear combination of this pair produces an orbital localized at the position of attack, and a second confined to the conjugated system exclusive of this position. Hund's rule⁷ requires the two available electrons to be placed one in each orbital, thus accounting for the provision of a free electron at the position of radical attack.

- ¹ G. W. Wheland and L. Pauling, *J. Am. Chem. Soc.*, **57**, 2086 (1935).
² C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **192A**, 16 (1947).
³ Fukui, Yonezawa, and Shingu, *J. Chem. Phys.*, **20**, 722 (1952).
⁴ Fukui, Yonezawa, Nagata, and Shingu, *J. Chem. Phys.*, **22**, 1433 (1954).
⁵ H. H. Greenwood, *J. Am. Chem. Soc.* (to be published).
⁶ C. A. Coulson, *Disc. Faraday Soc.* No. 2, 9 (1947).
⁷ C. A. Coulson, *Valence* (Clarendon Press, Oxford, England, 1952), pp. 36, 98.

Methyl and Phenyl Affinities of Aromatic Compounds

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MEASUREMENTS have recently been reported by M. Levy and M. Szwarc¹ of "relative methyl affinities" of a number of aromatic compounds. These quantities are, in fact, relative reactivities towards attack by methyl radicals arising from the decomposition of acetyl peroxide. It is of interest to note that the numerical values of the relative methyl affinities are very close to those of the relative rates of attack by phenyl radicals, arising from the decomposition of benzoyl peroxide and from other sources, on the same aromatic compounds. The measurement of these quantities, which in Levy and Szwarc's terminology could be called "relative phenyl affinities," has been reported by the present authors and their co-workers.²⁻⁹ The results of these investigations are summarized and, where the quantities are available, compared with the corresponding relative methyl affinities, in Table I.

The agreement between the values of the two quantities for naphthalene and for diphenyl is striking, and the values reported for pyridine are at least of the same order of magnitude.

As well as the relative rates of attack tabulated in Table I we have measured the ratios of the various isomers formed in the phenylation of the aromatic compounds, and from the two sets of

TABLE I.

Compound	Relative phenyl affinity	Relative methyl affinity
Benzene	1	1
Toluene	1.9	
<i>tert</i> -Butylbenzene	0.87	
<i>p</i> -di- <i>tert</i> -Butylbenzene	0.63	
Naphthalene	23.9	22
Diphenyl	4.0	5
Pyridine	1.04	3
Nitrobenzene	4.0	
Fluorobenzene	1.3	
Chlorobenzene	1.4	
Brombenzene	1.7	
Iodobenzene	1.8	
<i>p</i> -Dichlorobenzene	2.7	
<i>sym</i> -Trichlorobenzene	5.0	

measurements calculated partial rate factors representing the reactivities of the various individual positions in the aromatic nuclei in terms of the reactivity of any one position in benzene. The partial rate factors were compared with those computed from the results of molecular-orbital calculations by a number of workers,¹⁰⁻¹⁷ and the substantial agreement between theory and experiment noted. In addition, the increase in methyl (or phenyl) affinity with increasing conjugation in the aromatic system, which was pointed out by Levy and Szwarc, was also noted by the present authors.²

Extensions of this work to include other aromatic systems, and other aryl radicals, will be published later.

- ¹ M. Levy and M. Szwarc, *J. Chem. Phys.*, **22**, 1621 (1954).
² D. H. Hey and G. H. Williams, *Discussions Faraday Soc.*, **14**, 216 (1953).
³ Augood, Hey, and Williams, *J. Chem. Soc.* 2094 (1952).
⁴ Augood, Hey, and Williams, *J. Chem. Soc.* 44 (1953).
⁵ Augood, Cadogan, Hey, and Williams, *J. Chem. Soc.* 3412 (1953).
⁶ Cadogan, Hey, and Williams, *J. Chem. Soc.* 794 (1954).
⁷ Hey, Stirling, and Williams, *J. Chem. Soc.* 2747 (1954).
⁸ Cadogan, Hey, and Williams, *J. Chem. Soc.* 3352 (1954).
⁹ Hey, Pengilly, and Williams (to be published).
¹⁰ G. W. Wheland, *J. Am. Chem. Soc.*, **69**, 900 (1942).
¹¹ C. Sandorfy, *Bull. Soc. Chim.*, **16**, 615 (1949).
¹² C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc. (London)* **A193**, 447 (1948).
¹³ W. A. Brown, *Quart. Rev.*, **6**, 63 (1952).
¹⁴ P. Yvan, *Compt. rend.*, **229**, 622 (1949).
¹⁵ F. Seel, *Z. Elektrochem.*, **52**, 191 (1948).
¹⁶ F. Seel, *Z. Naturforsch.*, **3a**, 35 (1948).
¹⁷ Burkitt, Coulson, and Longuet-Higgins, *Trans. Faraday Soc.*, **47**, 553 (1951).

Invariance of Integrated Transmittance and Total Fractional Transmission with Experimental Slit Function*

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IT is well known to spectroscopists that the integrated transmittance and total fractional transmission are, in principle, independent of experimental slit width under the conditions usually satisfied in experimental work. A recent discussion of this problem for a triangular slit function has been given, for example, by Nielsen, Thornton, and Dale.¹ It is the purpose of the present note to re-examine this question in more general terms and to specify the requirements under which the experimental results are, in principle, independent of the experimental slit function.

Consider the spectral region between the wave numbers ω_1 and ω_2 ($\omega_1 < \omega_2$) which are selected in such a way that for $\omega \leq \omega_1 + \Delta\omega^*$ and for $\omega \geq \omega_2 - \Delta\omega^*$ the spectral absorption coefficient $P(\omega)$ vanishes. The functional form of $P(\omega)$ in the range $\omega_1 + \Delta\omega^* < \omega < \omega_2 - \Delta\omega^*$ is arbitrary. The spectral region from ω_1 to ω_2 is scanned with an instrument which can be described by a slit function $g(|\omega' - \omega|, b, c)$ such that the instrument responds to the wave number ω' when it is set at ω . The slit function is assumed to vanish for $|\omega' - \omega| \geq \Delta\omega^*$. The parameters b and c are dependent

on the nature of the instrument selected for study. Representative slit functions are triangular, trapezoidal, or Gaussian.¹

Let $I^0(\omega)$ represent the incident intensity, $I(\omega)$ is the transmitted intensity, $P(\omega)$ equals the spectral absorption coefficient, and X is the optical density. The integrated transmittance is then

$$\int_{\omega_1}^{\omega_2} T(\omega) d\omega = \int_{\omega_1}^{\omega_2} \left[\frac{\int_{\omega-\Delta\omega^*}^{\omega+\Delta\omega^*} I^0(\omega') \{ \exp[-P(\omega')X] \} g(|\omega'-\omega|, b, c) d\omega'}{\int_{\omega-\Delta\omega^*}^{\omega+\Delta\omega^*} I^0(\omega') g(|\omega'-\omega|, b, c) d\omega'} \right] d\omega. \quad (1)$$

For spectrographs with reasonable resolution the intensity $I^0(\omega')$ may be taken as constant in the wave number range $\omega - \Delta\omega^* \leq \omega' \leq \omega + \Delta\omega^*$, i.e., $I^0(\tau + \omega) = I^0(\omega)$ for $|\tau| \leq \Delta\omega^*$. Hence, introducing an appropriate change of variables and changing the order of integration, we find

$$\int_{\omega_1}^{\omega_2} T(\omega) d\omega = \left[\int_{-\Delta\omega^*}^{\Delta\omega^*} g(|\tau|, b, c) d\tau \right]^{-1} \int_{\omega_1}^{\omega_2} \left(\int_{-\Delta\omega^*}^{\Delta\omega^*} \{ \exp[-P(\tau + \omega)X] \} g(|\tau|, b, c) d\tau \right) d\omega = \left[\int_{-\Delta\omega^*}^{\Delta\omega^*} g(|\tau|, b, c) d\tau \right]^{-1} \times \int_{-\Delta\omega^*}^{\Delta\omega^*} g(|\tau|, b, c) \left(\int_{\omega_1+\tau}^{\omega_2+\tau} \{ \exp[-P(\omega)X] \} d\omega \right) d\tau. \quad (2)$$

However, since $|\tau| \leq \Delta\omega^*$ the stated requirements for $P(\omega)$ imply that

$$\int_{\omega_1+\tau}^{\omega_2+\tau} \{ \exp[-P(\omega)X] \} d\omega = \int_{\omega_1}^{\omega_2} \{ \exp[-P(\omega)X] \} d\omega. \quad (3)$$

Consequently Eq. (2) reduces to

$$\int_{\omega_1}^{\omega_2} T(\omega) d\omega = \int_{\omega_1}^{\omega_2} \{ \exp[-P(\omega)X] \} d\omega. \quad (4)$$

The experimental conditions which must be met in order to justify the use of Eq. (4) are seen to be the following: (a) if the slit function vanishes for $|\omega' - \omega| \geq \Delta\omega^*$ and $P(\omega)$ vanishes for $\omega \leq \omega_1^0$ and $\omega \geq \omega_2^0$, we must scan at least over the spectral range from $\omega_1 = \omega_1^0 - \Delta\omega^*$ to $\omega_2 = \omega_2^0 + \Delta\omega^*$; (b) the incident intensity $I^0(\omega)$ must be a slowly varying function of ω such that $I^0(\omega + \tau) \simeq I^0(\omega)$ for $|\tau| \leq \Delta\omega^*$.

The total fractional transmission of a spectral region T_R is defined by the relation

$$T_R = \frac{\int_{\omega_1}^{\omega_2} \left(\int_{\omega-\Delta\omega^*}^{\omega+\Delta\omega^*} I^0(\omega') \{ \exp[-P(\omega')X] \} g(|\omega'-\omega|, b, c) d\omega' \right) d\omega}{\int_{\omega_1}^{\omega_2} \left(\int_{\omega-\Delta\omega^*}^{\omega+\Delta\omega^*} I^0(\omega') g(|\omega'-\omega|, b, c) d\omega' \right) d\omega}. \quad (5)$$

Proceeding as before, it is readily seen that Eq. (5) becomes

$$T_R = \frac{\int_{-\Delta\omega^*}^{\Delta\omega^*} g(|\tau|, b, c) d\tau \int_{\omega_1+\tau}^{\omega_2+\tau} I^0(\omega) \{ \exp[-P(\omega)X] \} d\omega}{\int_{-\Delta\omega^*}^{\Delta\omega^*} g(|\tau|, b, c) d\tau \int_{\omega_1+\tau}^{\omega_2+\tau} I^0(\omega) d\omega}.$$

Hence, if $I^0(\omega)$ has the same values at corresponding points in the spectral ranges, $\omega_1 - \Delta\omega^* \leq \omega \leq \omega_1 + \Delta\omega^*$ and $\omega_2 - \Delta\omega^* \leq \omega \leq \omega_2 + \Delta\omega^*$, respectively, then

$$T_R = \frac{\int_{\omega_1}^{\omega_2} I^0(\omega) \{ \exp[-P(\omega)X] \} d\omega}{\int_{\omega_1}^{\omega_2} I^0(\omega) d\omega}, \quad (6)$$

provided the previously stated conditions are met for the slit function and absorption coefficient. The conclusion that $I^0(\omega)$ is arbitrary, except in the neighborhood of the ends of the integration interval, is interesting and physically plausible.

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¹ Nielsen, Thornton, and Dale, Revs. Modern Phys. **16**, 307 (1944).

² We must choose the integration interval larger by at least $\Delta\omega^*$ on either end than the range for which $P(\omega)$ is nonzero because, in principle, the spectrometer will show absorption when it is set within a range $\Delta\omega^*$ of the nearest absorbing region.

Microwave Spectrum and Planarity of the Ring of Trimethylene Oxide

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OUR interest in trimethylene oxide $\text{CH}_2-\text{CH}_2-\text{CH}_2$ stems

from the recent work in infrared and Raman spectroscopy which indicates that cyclobutane¹ probably has a puckered ring. In the four-membered rings, the classical ring strain would tend to make the ring planar, while the preferred staggered configuration of the hydrogens in internal rotation would tend to make the ring puckered. Trimethylene oxide, having fewer hydrogens, would have less tendency to have a puckered ring, and the microwave work was undertaken to attempt to determine whether or not the ring is planar and to determine the structure of the molecule.

The microwave spectrum has been investigated in the region from 16 to 42 kmc/sec. The spectrum is very rich, due to the occurrence of a large number of Q branch lines for the ground and excited ring bending vibrational states of the molecule. Several lines have been assigned to the ground and first excited states, and a few to the second and third. A list of transitions, rotational constants, and moments of inertia is given in Table I.

Planar trimethylene oxide would have approximately equally spaced vibrational levels with statistical weights of 7 and 9. The intensities of rotational transitions for the ground and excited vibrational states would be in the ratio of 7:9 $\exp(-E_1/kT)$:7 $\exp(-E_2/kT)$ —for $A \leftrightarrow B_a$ transitions and 9:7 $\exp(-E_1/kT)$:9 $\exp(-E_2/kT)$ —for $B_b \leftrightarrow B_c$ transitions, where E_1 and E_2 are the energy levels of the first two vibrational states. If the molecule were bent and the two positions were separated by a high potential barrier at the planar position, the vibrational levels would coalesce in pairs and the statistical weights of each pair would be the same. If the two minima were separated by a low barrier, the statistical weights would be the same as for a planar molecule but the separation of the ground and first excited vibrational levels would be much less than that for the first and second excited vibrational levels. In trimethylene oxide the intensities of four rotational transitions were measured for several vibrational states and the accuracy was sufficient to determine that the statistical weights were necessary (i.e., the vibrational levels are single levels), and that E_1 was approximately 60 cm^{-1} and that

TABLE I.

Ground vibrational state			First excited vibrational state		
A	12 045.2	Mc/sec	A	12 058.0	Mc/sec
B	11 734.0	Mc/sec	B	11 726.0	Mc/sec
C	6730.7	Mc/sec	C	6772.6	Mc/sec
I_A	41.96509	amuA ²	I_A	41.92082	amuA ²
I_B	43.07823	amuA ²	I_B	43.10776	amuA ²
I_C	75.10116	amuA ²	I_C	74.63631	amuA ²
Assigned transitions in Mc/sec					
Transition	Ground vibrational state		First excited vibrational state		
	Experimental	Calculated	Experimental	Calculated	
110-211	41 932.7	(41 932.7)	41 950.5	(41 950.5)	
111-212	31 926.0	(31 926.0)	32 043.4	(32 043.4)	
101-202	32 223.3	32 223.3	32 358.6	32 361.9	
000-101	18 465.0	18 464.7	18 498	18 498.6	
312-331	16 490.2	(16 490.2)	16 443.8	(16 443.8)	
422-441	17 268.2	17 268.3	17 283.2	17 284.1	
522-541	18 346.5	(18 346.5)	18 452.1	(18 452.1)	
632-652	26 081	26 080.6	25 928	25 925.9	
742-762	26 333	26 333.0	26 215	26 216.7	
752-772	24 592	24 593.2	24 240	24 240.6	
862-882	23 890	23 890.2	23 460	23 458.3	
852-872	26 725	26 724.7	26 665	26 668.1	
972-992	22 976	22 979.9			