

782. *The Configuration of the Transition State in Methyl-radical Additions.*

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The linear relation between localisation energy and $\log(\text{methyl affinity}/n)$, where n denotes the number of reactive centres, as well as the blocking effect due to methyl substituents, is taken as evidence that a specific C-CH₃ bond is formed in the transition state of methyl-radical additions. This means that the transition state represents a σ -complex rather than a π -complex. Studies of methyl affinities of pseudo-blocked compounds indicate that this bond is approximately perpendicular to the nodal plane, and not close-to-nodal-plane as was assumed in the earlier papers from this laboratory.

WE discuss here the structure of the transition state leading to the addition of methyl radicals to olefinic and aromatic molecules. The first problem is whether formation of a linkage between an attacking radical and a *whole* molecule of the substrate is the rate-determining step of the reaction, or whether the incipient formation of a particular CH₃-C bond takes place in the transition state. The first alternative corresponds to a transition state of the π -complex type, while the second requires formation of a σ -bond in the activated complex.

The formation of a π -complex in radical additions to olefins was proposed by several workers. For example, Steinmetz and Noyes,¹ following Noyes, Dickenson, and Schomaker,² claim formation of a π -complex in addition of iodine atoms to olefins. A similar idea was expressed by Goering and his co-workers³ who studied the addition of bromine atoms, and although modified, it was still partially upheld in the more recent publication⁴ dealing with addition of trichloromethyl radicals. Goering *et al.* based their argument on the observation of *trans*-addition; however, they point out that this observation may be also accounted for in terms of σ -complex formation.

The experimental data accumulated during the last six years in our laboratory strongly favour the second alternative. Thus, it was found by Coulson⁵ and by us⁶ that the rate constants for radical addition computed *per reactive centre* are linearly related to the localisation energy of such a centre. This relation was established for a series of unsubstituted aromatic hydrocarbons which vary in their reactivities* by a factor of more than 10⁴, and for a series of compounds characterised by a >C=CH_2 reaction centre, such as ethylene, butadiene, styrene, etc. The important point is that the linear relation is not obeyed if the experimentally determined rate constants *are not* divided by the number of reactive centres, and this points to the formation of a specific C-CH₃ bond in the transition state. The last point requires clarification. The symmetry of π -orbitals in benzene is such that the formation of a centrally symmetrical π -complex between a radical R \cdot and a molecule of benzene is impossible. Such a complex, if formed, associates R \cdot with a particular carbon-carbon bond. Hence, even if a π -complex is involved in a transition state, $n = 6$ for benzene, but for anthracene $n = 4$ and for ethylene $n = 1$. Usage of such values for n destroys the observed linear relation.

Further argument for this hypothesis comes from studies of methyl-radical addition to methyl-substituted hydrocarbons. It was shown^{6,7} that a methyl substituent located

* The term reactivity will be used in this paper in reference to the rate of addition of methyl radicals to the respective compound.

¹ Steinmetz and Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 4141.

² Noyes, Dickenson, and Schomaker, *J. Amer. Chem. Soc.*, 1945, **67**, 1319.

³ Goering, Abel, and Aycock, *J. Amer. Chem. Soc.*, 1952, **74**, 3588.

⁴ Goering and Sims, *J. Amer. Chem. Soc.*, 1955, **77**, 3465.

⁵ Coulson, *J.*, 1955, 1435.

⁶ Szwarc and Binks, *Theoretical Organic Chemistry, Kekulé Symposium*, 1958, Butterworths, London, p. 262.

⁷ Binks and Szwarc, *J. Chem. Phys.*, 1959, **30**, 1494.

on a non-reactive centre enhances slightly the reactivity of the hydrocarbon and that the hyperconjugation hypothesis accounts quantitatively for the observed enhancement. On the other hand, if a methyl substituent is located on a reactive centre, then the reactivity of the compound is reduced by a large factor (6—10). For example, the relative rate constants (methyl affinities) for methyl-radical addition to anthracene and its 1-methyl, 2-methyl, and 2,6-dimethyl derivative are approximately the same^{6,7} (355—400). However, if a hydrogen atom at one of the reactive (9- or 10-)positions of anthracene is substituted by a methyl group, the reactivity of the resulting compound (9-methylanthracene) is reduced to 190, which means that its reactivity is only half that of anthracene.^{6,7} When both hydrogen atoms are substituted by methyl groups, then the respective rate constant decreases drastically,^{6,7} reducing the methyl affinity of 9,10-dimethylanthracene to 60. From the experimental linear relation between methyl affinity and localisation energy, and from calculated localisation energies of the less reactive positions of anthracene, one calculates the combined reactivities of positions 1—8 to amount to 20. One can consider, therefore, the excess of the reactivity observed in 9,10-dimethylanthracene, which amounts to 40, as the reactivity of the “blocked” 9- and 10-positions. Thus, the “blocking” by methyl substituents reduces the reactivity by a factor of about 10. Additional examples illustrating the effect of “blocking” are listed in references 6 and 7.*

Knowing that a specific C—CH₃ bond is formed in the transition state, we may now investigate the configuration arising around the reactive centre in the addition process. The formation of the new C—CH₃ bond utilises one of the π -electrons of the olefinic or aromatic molecule. Hence, in view of the much greater possibility of overlap between the *p*-electron of the radical and the π -electron in the direction perpendicular to the nodal plane than in it, one might expect the incipient bond in the transition state to be perpendicular to the nodal plane of the molecule. The magnitude of the “blocking” effect, caused by a methyl group substituted on the reactive centre, is surprisingly large, and this was considered as evidence against this structure of the transition state. Further, it was found that with all the heterocyclic compounds investigated addition of methyl radicals never takes place to a heteroatom, even if the heteroatom replaces the most reactive carbon centre. The following two examples illustrate this point.

The reactivities of nitrogen-containing heterocyclic aromatic compounds are, on the whole, higher than that of the analogous isocyclic compounds. For example, the relative rate constants of methyl-radical addition to quinoline and isoquinoline are 13.4 and 15 respectively,^{8,9} while the corresponding rate constant for naphthalene is 9. Again, the rate constants of the addition to anthracene and 1-aza-anthracene are 390 and 550 respectively,⁹ but for acridine the rate constant is reduced to approximately one-half of the anthracene value,^{8,9} *i.e.*, to 200, and an even lower value of 107 was found for phenazine.^{7,9} From analysis of these data one concludes that methyl radicals do not add to nitrogen.†

A similar situation is found in a series of benzoquinones. The lowest localisation energy, and therefore the highest reactivity, is expected, and observed,¹⁰ for the terminal carbons of *p*-xylene—the isocyclic analogue of *p*-benzoquinone. However, investigations carried out in this laboratory¹¹ seem to indicate that the addition of methyl radicals takes place to the C=C centres and not to the C=O centres of quinones. Although this claim

* In this connection it should be noted that Kooyman (*Nature*, 1955, **175**, 598) investigated the addition of $\cdot\text{C}(\text{CH}_3)_2\text{CN}$ radicals to substituted 9-anthracenes. The blocking effect was observed, although the substituent has also an accelerating effect on position 10.

† The relatively high value of the rate constant of methyl-radical addition to phenazine reflects the substantial activation of the other less reactive positions of the molecule by the presence of two nitrogen atoms.

⁸ Levy and Szwarc, *J. Amer. Chem. Soc.*, 1955, **77**, 1949.

⁹ Binks and Szwarc, unpublished results.

¹⁰ Errede and Szwarc, *Quart. Rev.*, 1958, **12**, 301.

¹¹ Buckley, Rembaum, and Szwarc, *J.*, 1958, 3442.

appears to be contradicted by experimental findings of some workers¹² who isolated ethers from the products of reaction of quinone with some radicals, we feel that our conclusion is justified and confirmed by the synthetic findings of Fieser and Oxford.¹³

These observations led to the suggestion that in the transition state the added methyl radical is located close to the nodal plane,^{7,14} since it was believed that such a configuration of the transition state accounts for the magnitude of the steric effect due to the methyl substituent and for the lack of addition to a heteroatom owing to an increase in the repulsion caused by the lone pair of electrons. To test further this hypothesis we investigated now some pseudo-blocked compounds, *i.e.*, compounds containing substituents which should hinder the addition if it takes place in the nodal plane but which should have a negligible effect on the course of a vertical addition. 1,4,5,8-Tetramethylantracene and 1,4,5,8-tetramethylacridine exemplify such compounds and their reactivities, reported in this paper, show that the hypothesis of nodal addition is untenable. We have to conclude, therefore, that the direction of the new C-CH₃ bond formed in the transition state is, at least approximately, vertical to the nodal plane. This point emerges also from recent studies by Goering and Sims⁴ who demonstrated in some instances a *trans*-addition of radicals to 1-bromocyclohexene.

Results and Discussion.—Two samples of 1,4,5,8-tetramethylantracene were examined. The first was prepared by Aldrich Chemicals Company and purified before use by chromatography, crystallisation, and vacuum-sublimation; it showed a sharp m. p. (270°). The second sample was offered to us by Professor Hey (whom we thank), and after recrystallisation from ethanol it showed the same m. p. and mixed m. p. In addition we prepared 1,3,5,7- and 2,3,6,7-tetramethylantracenes¹⁵ to compare their reactivities with that of the pseudo-blocked 1,4,5,8-isomer.

1,4,5,8-Tetramethylacridine and of 4,5-dimethylacridine (methyl substituents on carbon atoms adjacent to nitrogen) were offered to us by Professor Newman (whom we thank) and used without purification.

Determination of methyl affinities was carried out in iso-octane solution at 65°, acetyl peroxide being used for generation of methyl radicals. The experimental technique is described, *e.g.*, in ref. 8. The results are summarised in the Table.

Although the methyl affinity of the pseudo-blocked 1,4,5,8-tetramethylantracene is somehow lower than that of the other two isomers and of the unsubstituted anthracene, the decrease is too small to justify the assumption of a close-to-nodal-plane approach. The results obtained in the acridine series are even more indicative, showing no difference, within experimental error, between the reactivity of the pseudo-blocked tetramethyl derivative and the non-blocked dimethyl derivative. One has to accept, therefore, a vertical, or nearly vertical, configuration of the transition state in methyl-radical addition. A "secondary" deuterium effect¹⁷ in methyl-radical addition provides further evidence, for the proposed transition state Ph·CD:CD₂ was found to be more reactive than Ph·CH:CH₂ towards CH₃ addition by about 8%.

The blocking effect of a methyl group might arise from repulsion between the hydrogen atoms of this group and those of the approaching methyl radical. The magnitude of the observed steric factor is 6—10, and, if it arises entirely from an increase in the activation energy, this would call for an activation energy increase of 1.2—1.5 kcal./mole. The steric repulsion energy is, therefore, not greater than the potential energy barrier for the rotation which may be as high as 3 kcal./mole and which results from a similar type of interaction.

The lack of addition to a nitrogen or oxygen centre probably results from the repulsion

¹² Cohen, *J. Amer. Chem. Soc.*, 1947, **69**, 1057; Bickel and Waters, *J.*, 1950, 1746; Apparicio and Waters, *J.*, 1952, 4666.

¹³ Fieser and Oxford, *J. Amer. Chem. Soc.*, 1942, **64**, 2060.

¹⁴ Bader, Buckley, Leavitt, and Szwarc, *J. Amer. Chem. Soc.*, 1957, **79**, 5621.

¹⁵ Ellison and Hey, *J.*, 1938, 1847.

Methyl affinities determined in iso-octane solution at 65°.

Mole %	CH ₄	CO ₂	k_2/k_1	Mole %	CH ₄	CO ₂	k_2/k_1 (CH ₄ /CO ₂)
1,4,5,8-Tetramethylanthracene (I)				4,5-Dimethylacridine			
0.000	0.133	0.170	—	0.000	0.538	0.680	—
0.255	0.074	0.168	289	0.000	0.538	0.671	—
0.365	0.071	0.167	228	0.107	0.476	0.704	166
0.507	0.059	0.174	258	0.213	0.427	0.720	159
1,4,5,8-Tetramethylanthracene (II)				0.426	0.331	0.695	157
0.000	0.313	0.418	—	0.533	0.302	0.699	157
0.023	0.304	0.430	250	0.746	0.261	0.701	152
0.103	0.252	0.420	243	0.852	0.238	0.701	156
	Average for sample (I) 258 ± 20				Average 158 ± 5		
	„	„	(II) 247				
1,3,5,7-Tetramethylanthracene				1,4,5,8-Tetramethylacridine			
0.000	0.188	0.264	—	0.000	0.532	0.657	—
0.067	0.158	0.273	353	0.000	0.532	0.670	—
0.071	0.157	0.292	363	0.074	0.490	0.685	145
0.101	0.148	0.282	380	0.074	0.490	0.687	149
0.118	0.139	0.290	363	0.149	0.458	0.692	133
	Average 364 ± 10			0.222	0.427	0.699	134
2,3,6,7-Tetramethylanthracene				0.296	0.397	0.715	144
0.000	0.187	0.266	—	0.371	0.369	0.712	141
0.042	0.163	0.271	372		Average 141 ± 5		
0.069	0.155	0.267	320		Acridine (average) 187 ± 5		
0.139	0.123	0.269	352		or ~240*		
	Average 348 ± 20						

* Depending on the analytical technique used.

between the *p*-electron of the approaching radical and the lone pair of electrons of the nitrogen or oxygen atom. This repulsion is not as great for the vertical approach as it would be for a close-to-nodal-plane approach; nevertheless it might be sufficiently great to reduce substantially the rate of addition. The importance of such a repulsion is shown by the example of the low bond-dissociation energy of fluorine, compared with that of other halogens; ¹⁶ *D*(F-F) is about 36 kcal./mole, *i.e.*, substantially lower than *D*(Cl-Cl), and greatly less than its extrapolated value of about 60 kcal./mole.

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¹⁶ Cottrell, "The Strength of Chemical Bond," Butterworths, London, 1958.

¹⁷ Matsuoka and Szwarc, unpublished results.