with increasing overvoltage. The escape of atomic hydrogen from the cathode to the MMA solution could result in the formation of a free radical with monomer and hence in polymerization. There is also, however, the possibility that reaction of monomer with atoms on the cathode surface and liberation of a radical to the solution may be involved according to the equation

$$\mathrm{MeH} + \mathrm{m} \rightarrow \mathrm{m}^* + \mathrm{Me}$$

where m^* is the liberated radical. Such a process should occur more readily than the evaporation of an atom of hydrogen by reason of the exothermicity q of the reaction between atomic hydrogen and a vinyl compound to form a radical. The energy quantity in the Boltzmann factor governing the process should be lessened by this amount q.

Acknowledgment.—I wish to express my grateful appreciation and thanks to Professor H. S. Taylor for his continuous interest and advice during the course of this work and for assistance in the preparation of the manuscript for publication.

Summary

Polymerization of methyl methacrylate can be initiated during the electrolytic reduction of aqueous solutions of the monomer. The efficiency of the process increases with increasing overvoltage of the cathode.

Metals loaded with hydrogen, either electrolytically or by processes of chemisorption, initiate polymerization of aqueous solutions of methyl methacrylate.

The efficiency of initiation is low compared with the total hydrogen released by electrolysis or present in the chemisorbed state.

Initiation gives rise to radicals which can continue to add monomer units away from the initiation center and over periods of hours, in the original electrolytic solution or in monomer solutions to which the electrolytic solution is added.

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[CONTRIBUTION NO. 495 FROM THE DEPARTMENT OF CHEMISTRY OF INDIANA UNIVERSITY]

Ultraviolet Absorption Spectra of 2-Substituted 8-Quinolinols

BY J. P. PHILLIPS,[1] W. H. HUBER,[1] J. W. CHUNG[1] AND L. L. MERRITT, JR.

In connection with an investigation of steric hindrance to chelate formation by substituents in the 2-position of 8-quinolinol[2,3] the ultraviolet absorption spectra of a number of 2-substituted 8-quinolinols were determined, since spectra can frequently be used to indicate the existence of steric hindrance to a planar structure caused by substituents.[4] All the compounds included in this study had been shown to exhibit steric hindrance, or at least hindrance from some source,[5,6] to the formation of a chelate with aluminum.

Information about the structure of these compounds in acid, base and neutral solvents was expected from the determination of their spectra, but in order to narrow down the number of possible structural feature-spectra associations the spectra of the 8-methoxy derivatives of most of these compounds were determined also.

Experimental

The preparation of these compounds has been previously described.[5]

The absorption spectra were determined with a Beckman model DU spectrophotometer from 225 to 400 mμ (unless otherwise indicated) using slit widths such that maxima could be located to the nearest 1–2 mμ. Solutions in the concentration range 10^{-3}–10^{-5} M were generally suitable; all the compounds obeyed Beer's law sufficiently well in this range. The accuracy of the molecular extinctions is estimated to be ±10% or better.

Since the spectra of these compounds were generally quite similar in shape to each other and to 8-quinolinol, graphs of which have appeared in the literature several times,[7,8] it was not considered desirable to present plots of our data here.

Results and Discussion

8-Quinolinol has a planar structure composed of three fused rings, one of them completed through a nitrogen–hydrogen bridge. A steric effect by a group in the 2-position sufficient to inhibit the formation of the bridge would make the third ring no longer co-planar with the quinoline nucleus and the consequent decrease in the number of resonance forms should produce a decrease in absorption and a shift to shorter wave lengths in the spectra. A comparison of 2-methyl-8-quinolinol with 8-quinolinol (Table I) and with 4-methyl-8-quinolinol shows that a shift to shorter wave lengths in the 2-substituted compound occurs in the absorption maxima labeled "4" in the tables, but not in the whole spectrum. Similar effects were noted in the copper chelates of these compounds (Table II). Evidence from spectra for steric hindrance in this case is not obtained.

A definite case of steric hindrance was observed from the spectra of 2-*o*-tolyl-8-methoxyquinoline (Table III); this compound absorbed at shorter wave lengths and less strongly than its meta and para isomers, undoubtedly indicating restricted rotation as in substituted biphenyls.[4] Perhaps because of this hindrance we were unable to pre-

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[1] Abstracted from parts of theses submitted by W. H. Huber and J. W. Chung in partial fulfillment of the requirements for master's degrees, and from a portion of the doctoral thesis of J. P. Phillips.

[2] Phillips and Merritt, THIS JOURNAL, **71**, 3984 (1949).

[3] Merritt and Walker, *Ind. Eng. Chem., Anal. Ed.*, **16**, 387 (1944).

[4] Pickett, Groth, Duckworth and Cunliffe, THIS JOURNAL, **72**, 44 (1950).

[5] Phillips, Elbinger and Merritt, *ibid.*, **71**, 3986 (1949).

[6] Irving, Butler and Ring, *J. Chem. Soc.*, 1489 (1949).

[7] Ewing and Steck, THIS JOURNAL, **68**, 2181 (1946).

[8] Stone and Friedman, *ibid.*, **69**, 209 (1947).

TABLE I

ABSORPTION MAXIMA IN ULTRAVIOLET SPECTRA OF 2-SUBSTITUTED 8-QUINOLINOLS[a]

2-Substituent	mμ(1)	mμ(2)	mμ(3)	mμ(4)
		A. In cyclohexane		
None		242(4.62)		320(3.38)
CH_3—		246(4.72)		309(3.46)
C_6H_5—		271(4.61)		321(3.63)
p-$CH_3C_6H_4$		276(4.69)		325(3.81)
p-$C_6H_5C_6H_4$ ·		290(4.69)		326–332(4.11)
p-CH_3O—C_6H_4—	243–244(4.23)	287(4.66)		330(3.95)
p-$C_2H_5OC_6H_4$—	244(4.23)	288–289(4.66)		332–336(3.99)
p-$(CH_3)_2NC_6H_4$—	251(4.41)	312–313(4.49)		362–366(4.32)
p-$(C_2H_5)_2NC_6H_4$—	250(4.45)	316(4.48)		370–372(4.40)
$C_6H_5CH{=}CH$—	226(4.16)	294(4.60) 302(4.62)		343(4.26)
m-$CH_3C_6H_4CH{=}CH$—	228(4.14)	295(4.62) 305–306(4.64)		345–346(4.34)
p-$CH_3OC_6H_4CH{=}CH$—	246–247(4.11) 262–265(4.08)	311–(4.59)		346–349(4.48) 355–358(4.48)
		B. In 0.1 *N* hydrochloric acid		
None		250(4.60)	318–319(3.23)	358(3.23)
CH_3—		255(4.64)	320(3.49)	345(3.23)
C_6H_5—	248(4.30)	282(4.61)	338(4.15)	
p-$CH_3C_6H_4$—	251(4.28)	290(4.40)	345(4.18)	
p-$(CH_3)_2NC_6H_4$—	278–279(4.63)	335(4.04)	444–448(3.60)	
$C_6H_5CH{=}CH$—	246(3.76) 264–266(3.81)	310(4.34)	372(4.40)	
m-$CH_3C_6H_4CH{=}CH$—	266–267(3.95)	310–312(4.41)	375–377(4.51)	
		C. In 0.1 *N* sodium hydroxide		
None		253(4.50)		345(3.43)
CH_3—		255(4.48)		335(3.48)
C_6H_5—		280–281(4.67)		371–376(3.48)
$C_6H_5CH{=}CH$—		308–310(4.32)		398(3.40)

[a] Figures in parentheses in these tables are the logarithms of the molecular extinction coefficients. [b] In 95% alcohol maxima occurred at 265–268(4.68) and 315–318(3.85).

TABLE II

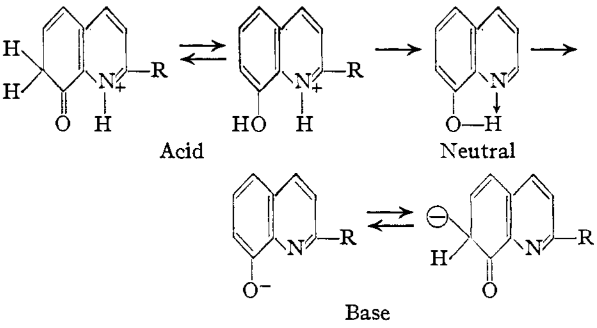
ABSORPTION MAXIMA IN ULTRAVIOLET SPECTRA OF COPPER CHELATES OF 2-SUBSTITUTED 8-QUINOLINOLS IN CHLOROFORM[a]

2-Substituent	mμ(1)	mμ(2)	mμ(3)	mμ(4)
None	262–263(4.65)		405–411(3.64)	
CH_3—	268–269(4.65)		392–396(3.62)	
C_6H_5—	281(4.74)		413–417(3.49)	
$C_6H_5CH{=}HC$—	318–319(4.83)		430–435(3.83)	

pare 2-*o*-tolyl-8-quinolinol by the method used for 2-*p*-tolyl-8-quinolinol,[5] that is, direct addition of *o*-tolyllithium to 8-quinolinol.

With increasing length of the conjugated system attached to the 2-position a bathochromic shift in the absorption maxima was noted as anticipated; there was also a fairly steady increase in amount of absorption for cyclohexane solutions in the maxima labeled "4." With some derivatives this bathochromic shift was sufficient to bring a new absorption band ("1") into the available experimental region. The effects produced by the auxochromic groups $-CH_3$, $-OR$ and $-NR_2$ also accorded with expectation; indeed, during the synthesis of this group of compounds the absorption spectra were of more aid in identifying the products than elemental analysis.

The changes in the spectra of the 8-quinolinols in going from acid to neutral to basic solvents can be plausibly explained on the basis of the structure changes



Since there can be no such structure changes for the 8-methoxyquinolines in going from neutral to basic solvents, there is no appreciable difference in the spectra of these compounds in cyclohexane and sodium hydroxide.

The maxima labeled "3" in the tables seem to be associated with the presence of a nitrogen–hydrogen bond, since they occur only in an acid medium. The remainder of the spectrum obtained in acid solution may conceivably be simply a shift of the neutral spectrum to longer wave lengths as a result of the increased number of resonating structures indicated by the equations above; this interpretation, however, fails to explain the disappearance of

Table III

Absorption Maxima in Ultraviolet Spectra of 2-Substituted 8-Methoxyquinolines^a

2-Substituent	mμ(1)	mμ(2)	mμ(3)	mμ(4)
		A. In cyclohexane		
CH_3—		242(4.62)		296(3.53)
C_6H_5—^{b}		266		318
o-$CH_3C_6H_4$—		261(4.56)		306(3.75)
m-$CH_3C_6H_4$—		268–269(4.69)		316–319(3.87)
p-$CH_3C_6H_4$—		271(4.71)		322(3.93)
p-ClC_6H_4—		271(4.79)		320(4.04)
$C_6H_5CH{=}CH$—		288–289(4.57) 298(4.57)		341(4.30)
		B. In 0.1 *N* hydrochloric acid		
CH_3—		254(4.70)	318(3.54)	345(3.26)
C_6H_5—	250(4.23)	282(4.61)	337(4.23)	
o-$CH_3C_6H_4$—	253(4.52)	280(4.26)	331(3.97)	
m-$CH_3C_6H_4$—	251(4.20)	284(4.53)	340(4.18)	
p-$CH_3C_6H_4$—	252(4.36)	289(4.48)	344(4.28)	
p-ClC_6H_4—	252–253(4.26)	288(4.53)	340(4.23)	
$C_6H_5CH{=}CH$—	246(3.87) 264–266(3.93)	308(4.48)	372(4.53)	

maximum "4" in a number of the compounds in acid solution.

Support for the hypothesis that metal chelate rings are quite similar in character to the rings formed by hydrogen bridges in the original chelate forming reagent[9] is illustrated by the close resemblance of the sodium and copper salts of the 8-quinolinols to the unsubstituted compounds in neutral solvents (Tables I and II). The only significant difference is a considerable bathochromic shift in passing from the reagent to the sodium salt to the copper chelate, as would be anticipated from the increasingly complex structure of the hydrogen, sodium and copper ions.

Except for a general small hypsochromic shift the spectra of the 8-methoxyquinolines in neutral and acid solvents are virtually identical with the 8-hydroxy analogs.

Summary

The ultraviolet absorption spectra of a group of 2-substituted 8-quinolinols and their 8-methoxy derivatives have been determined in various types of solvents and some tentative associations of structure and spectra made. Evidence for steric inhibition of chelate formation by 2-substituents was not obtained.

Bloomington, Indiana Received July 31, 1950

[9] Calvin and Wilson, This Journal, **67**, 2003 (1945).

[Contribution from the George Herbert Jones Laboratory of the University of Chicago]

Reactions of Atoms and Free Radicals in Solution. XXIV. The Reactions of Acetyl Peroxide with Chloro- and Dichloroalkanes[1]

By M. S. Kharasch and G. Buchi

Objectives of the Present Study.—Earlier studies in this Laboratory have indicated that hydrocarbons and halogenated hydrocarbons vary widely in the facility with which they yield hydrogen or halogen atoms to free methyl radicals, forming methane or a methyl halide and a derivative free radical. In a given molecule one (or one of several equivalent) atoms is usually much more susceptible to methyl-radical abstraction than are the others; in such cases it is possible to specify in advance the derived free radical that will result preferentially or exclusively from methyl-radical attack.

On the basis of previous observations it is possible to state that, as points of methyl-radical attack, tertiary hydrogen atoms take preference over secondary hydrogen atoms, which in turn take preference over primary hydrogen atoms. It has already been shown that methyl radicals abstract preferentially the hydrogen atom of chloroform, one of the bromine atoms of bromoform and the bromine atom of bromotrichloromethane. On this basis, however, no general statement regarding the relative labilities of hydrogen and halogen atoms is justifiable, nor can confident prediction be made as to which of two like but dissimilarly located halogen atoms will prove the more susceptible to methyl-radical attack. One of the objectives of the present study was to cast additional light on these points.

It is further known from previous observation that derived free radicals (formed by the attack of methyl radicals on hydrocarbons or halogenated hydrocarbons) vary widely in their tendencies to (1) react with other components of the reaction system, or (2) react with each other by (a) disproportiona-

[1] The authors wish to acknowledge the generous support of the Firestone Tire and Rubber Company which made this research possible.