molecule calculated as an additive quantity.[24] With the exception of the porphyrazines, the solute molecules in Table III have volumes slightly more than twice that of the solute, *e.g.*, anthrone, 184 × 10^{-24} cc., phenanthrenequinone, 188 × 10^{-24}, and benzene, 84 × 10^{-24}. These volumes lead to calculated relaxation times at 20° of 86 × 10^{-22} sec. for anthrone and 88 × 10^{-12} for phenanthrenequinone, slightly lower than the values in Table III calculated by means of eq. 9 but still much higher than the observed values. These discrepancies and those for the remaining solutions in Table III, other than the porphyrazines, resemble those found by Meakins for other solutions in about the same range of solute-to-solvent molecular volume ratios. The volume of the metal-free porphyrazine molecule is calculated from "atomic increments"[24] to be 881 × 10^{-24} cc., about 10.5 times that of the solvent molecule. This gives a calculated value 410 × 10^{-12} sec., in much better agreement with the observed 302 × 10^{-12} than any of the calculated values in Table III, an agreement which is consistent with the conclusion of Meakins. The ferric porphyrazine molecule, having about the same volume, should have about the same relaxation time according to the simple Debye equation, but the observed value is much larger, probably, because of the extensive displacement of solvent molecules involved in the rotation out of the molecular plane. The observed value is, however, nearer to the value calculated by the Debye equation than it is to that calculated with eq. 9. It is evident that, for these solutions as for those investigated by Meakins, the agreement with observed values given by eq. 9 is better for small molecules but poorer for large molecules than that given by the Debye theory.

PRINCETON, NEW JERSEY

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[24] J. T. Edward, *Chem. and Ind.*, 774 (1956).

[CONTRIBUTION FROM THE MEMORIAL UNIVERSITY OF NEWFOUNDLAND]

Electronic Spectra and Molecular Dimensions. III.[1] Steric Effects in Methyl-substituted α,β-Unsaturated Aldehydes

BY W. F. FORBES AND R. SHILTON

RECEIVED JUNE 2, 1958

The spectra of acrolein and of its methyl-substituted analogs are investigated. The compounds provide examples of some of the simplest conjugated systems in which steric interactions can be detected, and the spectra are therefore discussed with reference to current theories of steric effects in electronic spectra. Previously obtained effective interference radii for atoms in solution, as determined for aromatic systems, provide a consistent interpretation of steric effects in this series.

Introduction

Earlier parts of this series have shown how a steric interpretation of certain spectral effects[2] may be used to obtain values for the effective interference radii of atoms in solution. Examples were then chosen from aromatic compounds. In order to be able to extend the argument to aliphatic conjugated systems, the spectra of acrolein and of its methyl-substituted analogs have been determined. Acrolein provides one of the simplest examples of a conjugated system, and methyl-substituents are known frequently to cause appreciable steric interactions.

Previous work on the spectral properties of α,β-unsaturated carbonyl compounds includes the development of some useful relations concerning the positions of maximal wave length in the ultraviolet region.[3] The effect of structure on the extinction coefficients is less well understood, but it has been assumed that the maximal extinction coefficient ($\epsilon_{\max}$) differs depending on whether the system exists in the *s-cis* or *s-trans* conformation[4] (for nomenclature used, see ref. 5).

Experimental

The ultraviolet absorption spectra were determined at least in duplicate by standard methods in 1 cm. and 2 mm. quartz cells using a Unicam SP500 spectrophotometer. Some of the values were also checked on a Beckman Model DU spectrophotometer and on another SP500 spectrophotometer. The absorption curves obtained in cyclohexane media are shown in Fig. 1.

Since the band shapes are similar for the series of compounds shown in Fig. 1, the extinction coefficients at maximal absorption ($\epsilon_{\max}$) are used as a semi-quantitative measure of the actual absorption intensities. The similarity of band shape as shown in Fig. 1 for solutions in cyclohexane is also obtained for solutions in ethanol. The values of $\lambda_{\max}$ and $\epsilon_{\max}$ are listed in Table II. Most of the spectra have been reported previously, but frequently our values are not in good agreement with the reported data. We attribute previous low values to instrumental and weighing errors; our values are in good agreement with recent determinations. The only satisfactory weighing technique we could find was that of Forbes and Mueller.[6] The precision of $\lambda_{\max}$ values is estimated to be ±0.5 mμ, and the precision of $\epsilon_{\max}$ values ±5% or better. Values were reproducible in most cases to ±2%. Intensities can therefore be considered satisfactory for comparison purposes, since the data were obtained under identical conditions.

It was also found that the spectrum of a solution of crotonaldehyde in ethanol remained unaltered on standing for 24 hr. and showed only a 3% drop in $\epsilon_{\max}$ on standing for 14 days. This indicates that no formation of hemiacetal takes place, and this view also receives support since addition of small amounts of hydrochloric acid to the solution, which may facilitate hemiacetal formation, causes an immediate decrease in the absorption intensity.

All the compounds used were commercially available or prepared by methods as described in the literature. After

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[1] Part II, THIS JOURNAL, **79**, 6495 (1957).

[2] W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **35**, 488 (1957), and preceding papers in that series.

[3] (a) R. B. Woodward, THIS JOURNAL, **63**, 1123 (1941); (b) **64**, 76 (1942); (c) L. K. Evans and A. E. Gillam, *J. Chem. Soc.*, 565 (1943).

[4] R. B. Turner and D. M. Voitle, THIS JOURNAL, **73**, 1403 (1951).

[5] W. F. Forbes and W. A. Mueller, *Can. J. Chem.*, **34**, 1347 (1956).

[6] W. F. Forbes and W. A. Mueller, *ibid.*, **34**, 1542 (1956).

fractionation in the presence of hydroquinone, the compounds possessed physical properties as shown in Table I.

TABLE I

PHYSICAL PROPERTIES OF α,β-UNSATURATED ALDEHYDES

Compound	B.p., °C. (mm.)	Refractive index		Source
Acrolein (I)	51 (769)	$n^{24.5}_D$	1.3974	[a]
Crotonaldehyde (II)	26 (30)	n^{25}_D	1.4347	[a]
β-Methylcrotonaldehyde (III)		n^{20}_D	1.4548	[b]
α-Methacrolein (IV)	62 (752)	n^{22}_D	1.4100	[c,d]
Tiglaldehyde (V)	49 (76)	n^{20}_D	1.4480	[a]
2,3-Dimethylbut-2-enal (VI)	41 (8)[9]	n^{18}_D	1.4704[9]	[e]
Cyclohexylideneacetaldehyde (VII)	104 (25)	n^{22}_D	1.4980	[f]

[a] Eastman Kodak Co. [b] Kindly supplied by Messrs. Hoffmann-La Roche and Co., Basle, Switzerland. [c] Carbide and Carbon Chemicals Co. [d] Reported constants for this compound vary widely: *e.g.*, Handbook of Chemistry and Physics[7] gives b.p. 73.5°, 760 mm., n^{20}_D 1.4191 and Rogers[8] reports b.p. 66.5°, 752 mm., n^{25}_D 1.4098. [e] Prepared by the method of Braude and Evans.[9] [f] We are indebted to Professor M. Viscontini of Zürich University for a generous sample of this compound.

The Ultraviolet Absorption Spectra of α,β-Unsaturated Aldehydes.—The main absorption maxima of the α,β-unsaturated aldehydes are listed in Table II.

TABLE II

MAIN ABSORPTION MAXIMA OF METHYL-SUBSTITUTED ACROLEINS IN ETHANOL AND IN CYCLOHEXANE SOLUTION

Compound	Solvent, cyclohexane		Solvent, ethanol	
	λ_{max} (mμ)	ϵ_{max}	λ_{max} (mμ)	ϵ_{max}
[CH_2=CH·CHO (I)	203	12,000	207	11,200]
CH_3·CH=CH·CHO (II)	213	17,300	218	17,900
$(CH_3)_2C$=CH·CHO (III)	228	11,400	235.5	11,900
CH_2=C(CH_3)·CHO (IV)	213	11,100	216	11,000
CH(CH_3)=C(CH_3)·CHO (V)	222.5	16,700	226	16,100
$(CH_3)_2C$=C(CH_3)·CHO (VI)	240	13,500[a,b]	245	13,000[a]
[Cyclohexylideneacetaldehyde (VII)	231.5	16,000[a,c]	238	16,000][a,c]

[a] Intensities are estimated from the purity of the sample as determined by chromatographic estimation of the 2,4-dinitrophenylhydrazone. [b] *Cf.* ref. 10. [c] *Cf.* ref. 11.

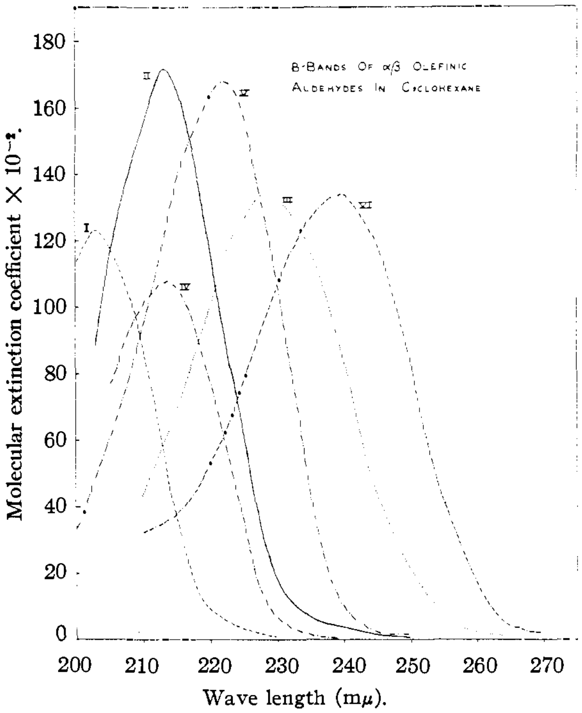
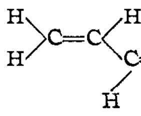


Fig. 1.—Absorption curves for the following compounds in cyclohexane: (i) CH_2=CH·CHO (I); (ii) CH_3CH=CH·CHO (II); (iii) $(CH_3)_2C$=CH·CHO (III); (iv) CH_2=C(CH_3)·CHO (IV); (v) CH(CH_3)=C(CH_3)·CHO (V); (vi) $(CH_3)_2C$=C(CH_3)·CHO (VI).

The conformation of acrolein recently has been investigated by microwave spectroscopy[12] and the predominant structure was found to be *s-trans* (IA); this confirmed earlier conclusions based on dipole moment data,[13] which also suggested the conformation IA. Wagner, *et al.*,[12] estimated the contribution of the *s-cis* conformation to be only about 2% at room temperature, and the energy difference between the two conformations is estimated to be 2.5 kcal./mole. Similar small values for the energy difference have been deduced by de Groot and Lamb[14] from ultrasonic absorption spectra. The infrared spectra are also of interest because in the gaseous phase the carbonyl band of acrolein is reported[15] to occur as a doublet at 1733 and 1714 cm.$^{-1}$. It is therefore possible that the carbonyl band at 1733 cm.$^{-1}$ corresponds to the *s-cis* conformation.



IA

There is no reason to suspect that crotonaldehyde exists less predominantly than acrolein in the *s-trans* conformation[9,13]; in fact, one might expect even greater preference for that conformation in crotonaldehyde. Evidence for additional resonance stabilization because of the β-methyl group is provided by dipole moment data,[8,13] ultrasonic absorption spectra[14] and infrared spectra.[15,16] The displacement to longer wave length of the absorption band in the ultraviolet region can similarly be interpreted as evidence for additional resonance stabilization. This displacement is parallel to the displacement of the infrared carbonyl band to lower frequency observed in CCl_4 solution for crotonaldehyde, compared with acrolein. Structures of type IIA would be expected to contribute appreciably to the resonance interaction, since on the

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[7] "Handbook of Chemistry and Physics," 35th Ed., Ed. C. D. Hodgman, *et al.*, Chemical Rubber Publishing Co., Cleveland, Ohio, 1953.

[8] M. T. Rogers, THIS JOURNAL, **69**, 1243 (1947).

[9] E. A. Braude and E. A. Evans, *J. Chem. Soc.*, 3334 (1955).

[10] E. S. Waight and R. L. Erskine, "Absorption Spectra of Conjugated Carbonyl Compounds" in "Steric Effects in Conjugated Systems" Butterworths, London, 1958, in press.

[11] J. B. Aldersley, G. N. Burkhardt, A. E. Gillam and N. C. Hindley, *J. Chem. Soc.*, 10 (1940).

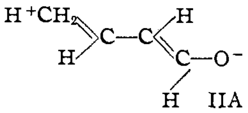
[12] R. Wagner, J. Fine, J. W. Simmons and J. H. Goldstein, *J. Chem. Phys.*, **26**, 634 (1957).

[13] J. B. Bentley, K. B. Everard, R. J. B. Marsden and L. E. Sutton, *J. Chem. Soc.*, 2957 (1949).

[14] M. S. de Groot and J. Lamb, *Proc. Roy. Soc.* (*London*), **A242**, 36 (1957).

[15] D. Cook, THIS JOURNAL, **80**, 49 (1958), and private communication.

[16] *Cf.* L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1954, p. 117.

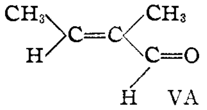

IIA

basis of such structures all the above-mentioned effects can be rationalized.[8,13,14]

The introduction of a second β-methyl group to afford β-methylcrotonaldehyde will presumably not lead to any great change in the proportion of *s-trans* conformations in this series, and in fact the compound has been thought to exist in that conformation.[10] A definite decrease in ϵ-value is observed for compound III compared with compound II and this decrease, on the basis of previously discussed considerations,[1] is ascribed to a steric effect. We return to this point later.

α-Methacrolein (IV) compared with acrolein (I) shows a wave length displacement (see Table II) as would be anticipated from Woodward's correlations.[3a,b,17] A tendency for an increased proportion of *s-cis* conformations might be expected from steric considerations and this is in fact suggested from dipole moment and infrared data. Thus, α-methacrolein has a dipole moment of 2.72 Debye units, compared with 2.88 Debye units for acrolein.[8,13] The carbonyl frequency of α-methacrolein in carbon tetrachloride is 1702 cm.$^{-1}$ (ϵ^a 240) and the olefinic frequency is 1637 cm.$^{-1}$ (ϵ^a 16).[18] These latter figures are close to those for *s-cis* compounds,[10] and in this way both infrared and dipole moment data confirm the hypothesis that α-methacrolein exists to an appreciable extent in *s-cis* and/or non-planar *s-trans* conformations.

The wave length displacement for tiglaldehyde (V), compared with α-methacrolein (IV), is as anticipated, *ca.* 10 mμ (see Table II), very similar to the wave length displacement observed between crotonaldehyde (II) and acrolein (I). This suggests that the β-methyl substituent again exerts its usual effect, that is, the substituent facilitates the formation of various dipolar resonance forms. The predominant conformation is presumably as shown in VA, although the *s-cis* isomer, and other non-planar forms, may contribute to a limited extent to the actual ground state conformations of the molecule. The presence of conformations other than planar *s-trans* isomers is also indicated by the reported dipole moment of 3.39 Debye units for tiglaldehyde compared with the dipole moment of 3.54 Debye units for crotonaldehyde.[8,13]


VA

The wave length displacements in cyclohexane and ethanol for 2,3-dimethylbut-2-enal (VI) compared with V are 17.5 and 19 mμ, respectively, comparable to the wave length displacements observed between II and III, which are 15 and 17.5 mμ in cyclohexane and ethanol, respectively.

The pronounced intensity decrease for compound VI compared with compound V again shows the operation of steric interactions. Waight and Erskine[10] have drawn attention to the fact that the infrared C=O and C=C bands are of nearly equal intensity in *s-cis* compounds but that the C=C band is much weaker in *s-trans* structures. For compound VI the ratio of the apparent extinction coefficients of the infrared C=O band over the infrared C=C band is reported to be $\epsilon_{C=O}/\epsilon_{C=C}$ = 374/122.[10] The data quoted above then may be taken to suggest that compound VI exists predominantly in a planar *s-trans* conformation, but also to a limited extent in other conformations which are planar or non-planar *s-cis*.

The wave length displacements observed on changing the solvent from cyclohexane to ethanol remain fairly constant to a first approximation ($\Delta\lambda$ = 3-7.5 mμ; see Table II). Only for two compounds, crotonaldehyde (II) and β-methylcrotonaldehyde (III), is the displacement to longer wave length accompanied by an increased extinction coefficient. In these two compounds the *s-trans* conformation would be expected to contribute more extensively than in the other four compounds; hence it is tempting to assume that in these other four compounds (I, IV, V, VI), where the tendency for *s-trans* coplanarity is less strong, additional steric interactions due to carbonyl group solvation in ethanol tend to force the molecule into non-planar conformations. In this connection it may also be noted that the wave length displacements between cyclohexane and ethanol appear to be smaller in compounds where solvent molecules are tentatively assumed to contribute to the steric interactions (see Table II).

Steric Effects in α,β-Unsaturated Aldehydes.—The observed steric interactions may be discussed under two headings. First, there are spectral effects which may be ascribed with a considerable degree of confidence to steric interactions. Examples of these are provided by the spectra of β-methylcrotonaldehyde (III) and 2,3-dimethylbut-2-enal (VI). Secondly, some other spectral effects are only tentatively ascribed to steric interactions. Examples are the relatively low extinction coefficient of acrolein (I) and tiglaldehyde (V) compared with the extinction coefficient of crotonaldehyde (II) or the relatively low extinction coefficient in ethanol of compounds I, IV, V, VI. However, the evidence for steric interactions in this second group of compounds is much less definite.

If the spectrum of β-methylcrotonaldehyde (III) in cyclohexane represents an example of steric interaction, it is of interest to discuss this example, since the compound represents one of the simplest molecules in which steric inhibition of conjugation can be studied by ultraviolet absorption spectroscopy. Following our previous classification of steric effects[19] the spectral effect in β-methylcrotonaldehyde can *either* be regarded as a type I steric effect, that is, an intensity decrease occurs without appreciable wave length displacement;

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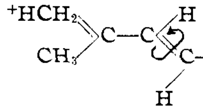
[17] It might be noted, as pointed out by a referee of this paper, that the bathochromic displacements for this type of compound cannot readily be explained on the basis of additional classical resonance structures.

[18] C. J. Timmons, private communication.

[19] W. F. Forbes, "The Classification of Steric Effects in Ultraviolet Absorption Spectra" in "Steric Effects in Conjugated Systems," Butterworths, London, 1958, in press.

or it may be regarded as a type II steric effect in which there is observed a bathochromic wave length displacement, compared with a hypothetical planar reference compound. However, it seems unlikely that a type II steric effect is involved because resonance forms of type IIIA will contribute appreciably to the excited state and hence a hypsochromic wave length displacement would be anticipated. This general argument is also indirectly supported by the ultraviolet spectrum of cyclohexylideneacetaldehyde (VII), which in cyclohexane absorbs maximally at 231.5 mμ (ϵ 16,000) (see Table II). The wave length displacement and decrease of intensity in the spectrum of III, compared with the spectrum of VII, may be associated with increased steric interaction in the former compound. As anticipated, the observed wave length displacement in the spectrum of III, compared with the spectrum of VII, is a *hypsochromic wave length displacement*, the band shapes remaining similar.



IIIA

If then, as seems probable, the observed spectral effect for β-methylcrotonaldehyde (III) represents a type I steric effect, it is of interest to use this example to discuss the nature of the type I steric effect. Before proceeding to do this, however, it may be noted that the spectra of β-methylcrotonaldehyde (III) and 2,3-dimethylbut-2-enal (VI) provide further examples of type I steric effects.

Type I steric effects were first discussed by Braude,[20] who proposed that type I effects may be caused by some molecules, at any one time, existing in ground states in which certain transitions to the electronic excited state are not possible. To account for the observation that no wave length displacement occurs, Braude proposed that the molecule also assumes distorted conformations from which the transition energy to the electronic excited states remains practically unaltered. This mechanism has been criticized by Waight and Erskine,[10] who claim that certain temperature effects make Braude's mechanism very unlikely.

Our view is that this criticism does not rule out Braude's general hypothesis but draws attention to the uncertainty involved in drawing energy diagrams. We believe that Waight and Erskine's temperature effects may be rationalized by merely drawing the schematic energy diagrams in a slightly different manner. However, we also believe that Braude's views may be usefully extended by considering not only one particular *s-cis* or *s-trans* conformation for which various vibrations and rotations are possible, but by considering also other conformations which may not contribute appreciably to the observed absorption but which nevertheless are present in significant amount. As an ideal hypothetical example,[5] we may consider a molecule which exists to an equal extent in *s-cis* and *s-trans* conformations, in which the energy levels and transition probabilities of the ground states are similar. If, for steric reasons, transitions are only possible for one of the two *s-cis* or *s-trans* forms, the absorption intensity will evidently be halved.

In the example of β-methylcrotonaldehyde (III) this then implies that on the basis of Braude's hypothesis we would assume that the molecule is not planar in the ground state or, more precisely, that the energy minimum of the molecule does not coincide with a value of zero for the interplanar angle. The interplanar angle referred to is the angle of twist as shown in IIIA. The reason why this variable is chosen arises from the consideration that appreciable steric interactions will presumably be most readily reduced by an increase in this angle.[21] The relevant energy diagrams relating energy to interplanar angle in β-methylcrotonaldehyde may be schematically represented as shown in Fig. 2.

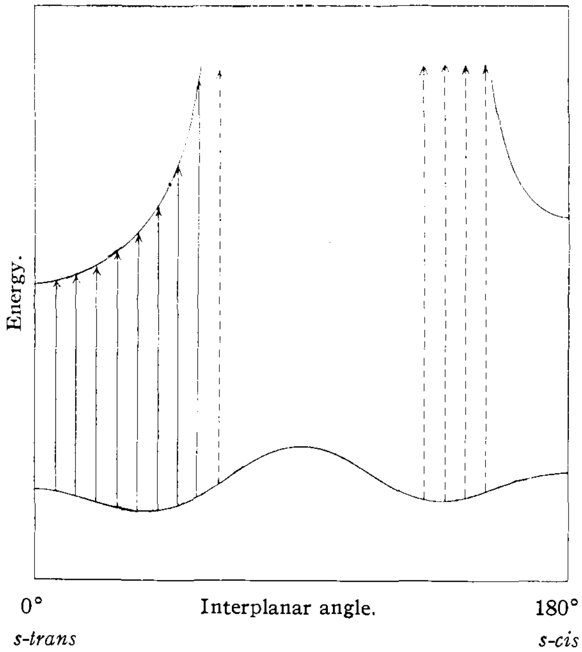


Fig. 2.—Schematic representation of electronic transitions between ground and excited states in β-methylcrotonaldehyde (III).

Figure 2 shows that β-methylcrotonaldehyde is assumed to exist in a number of ground states, which represent conformations mostly *s-trans* but also a smaller proportion of approximately *s-cis* conformations. From some states in both conformations transition leading to the observed absorption band are impossible or negligible.

Two additional points may be noted. First, Fig. 2 does not imply that the different energy levels correspond only to quantized twisting vibrations, since other vibrations and rotations may also contribute to energy levels which permit the molecule to exist, with unspecified probability, in conformations other than those possessing minimum energy. Secondly, Fig. 2 illustrates that it may not be possible to predict whether an increase in temperature will lead to an absorption intensity decrease or increase. This follows, because for the energy levels of β-methylcroton-

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[20] E. A. Braude and F. Sondheimer, *J. Chem. Soc.*, 3754 (1955).

[21] C. A. Coulson, private communication.

aldehyde, as drawn in Fig. 2, increasing the temperature may cause an increase in the permitted *s-trans* conformations for which transitions are no longer possible, and consequently the absorption intensity may decrease. *Alternatively*, increasing the temperature may cause an increase in the permitted *s-cis* conformations, so that transitions, which previously were not possible, are now possible for these conformations. The latter transitions may in this way give rise to an overall intensity increase, or a combination of the two opposing effects may lead to results which cannot be predicted *a priori*.

The Effective Interference Values of Atoms in Solution.—If steric interactions cause the observed spectral effects in β-methylcrotonaldehyde (III), they may be expected to be greater in the *s-trans* conformation (III A). Using scale drawings, the distance between the centers of the methyl group and the hydrogen atom in the coplanar *s-trans* form and the distance between the methyl group and the carbonyl oxygen atom in the *s-cis* form are both found to be 2.6 Å. From the previously suggested interference radii for H, 0.95 ± 0.1 Å.; O(in C=O), 1.0 ± 0.15 Å.; and CH_3, 1.7 ± 0.2 Å.[1,6]; it follows that if a hydrogen atom and a methyl group approach each other to within a distance of *ca.* 2.65 Å., one would expect spectral effects to be caused by these steric interactions. Precisely these spectral effects are observed. It may be noted that since the spectral effects ascribed to steric interactions are appreciable for β-methylcrotonaldehyde, it is probable that yet smaller steric interactions between non-bonded atoms may also be detected by this method.

It may finally be noted that throughout the discussion, by using the obvious important resonance forms, it has been assumed that the transitions involve an electron transfer in which a π-electron is transferred from one part of the molecule to another part of the molecule. This type of transition has been described as occurring to electron transfer (E.T.) states,[22] in order to distinguish it from transitions occurring to locally excited (L.E.) states in which the π-electrons remain associated with the C=C and C=O groups, respectively. Steric effects in spectra leading to E.T. states have also been discussed from a theoretical viewpoint by Murrell,[23] who tentatively concludes that steric hindrance for compounds of that type results in a decreased absorption intensity without displacement of the band position. This agrees with our conclusions. The reason why the absorption bands are ascribed by us to transitions leading to E.T. states, or at least to excited states in which electron transfer plays an important part, is based on the observation that for α,β-unsaturated carbonyl compounds large bathochromic wave length displacements are observed compared with the C=C and the C=O absorptions. In addition, not only for these, but also for other examples particularly in the aromatic series, displacements to longer wave length are greatest whenever the excited state is hybrid involving electron mobility along an extended conjugated system. Further, in this particular example, since the absorption band at 240 mμ for acetophenone is associated with transitions to an E.T. excited state,[23] it seems highly probable that a similar transition accounts for the absorption of ultraviolet light of α,β-unsaturated aldehydes.

Acknowledgments.—The authors gratefully acknowledge the receipt of research grants from the National Research Council of Canada and the Research Corporation of New York.

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[22] H. C. Longuet-Higgins and J. N. Murrell, *Proc. Phys. Soc.*, **68A**, 601 (1955); *cf.* also ref. 10.

[23] J. N. Murrell, *J. Chem. Soc.*, 3779 (1956).

ST. JOHN'S, NEWFOUNDLAND, CANADA

[CONTRIBUTION FROM E. I. DU PONT DE NEMOURS AND CO., SAVANNAH RIVER LABORATORY, AIKEN, SOUTH CAROLINA]

Kinetics of HNO_2 Catalyzed Oxidation of Neptunium(V) by Aqueous Solutions of Nitric Acid[1]

BY T. H. SIDDALL, III, AND E. K. DUKES

RECEIVED MAY 13, 1958

It was shown that the rate-controlling step of the oxidation reaction in the system occurs by reaction 1. Succeeding steps are suggested by reactions 2 and 3. Reaction 1 has an activation energy of 12 kcal. The number of hydrogen ions, n, which are involved may be as large as four. The rate of the reaction depends on the fourth power of the concentration of nitric acid. The rate of reaction 2 does not become comparably slow until the concentration of nitrous acid in the aqueous phase is reduced to less than 5×10^{-5} *M*. Equilibrium data were obtained for the over-all reaction 4. The over-all reaction is slightly endothermic. Equilibrium data are given in Table IV. Depending on the composition of the aqueous phase, the major fraction of the neptunium may be in the hexavalent state at equilibrium.

Introduction

Half cell potentials[2] show that nitrate ion should significantly oxidize Np(V) to Np(VI). However, the nitrate ion is known to be inert even when a thermodynamic potential exists. The first objective of the work covered in this paper was to investigate the kinetics of the oxidation of tracer concentrations (10^{-6} to 10^{-5} *M*) of Np(V) to Np(VI) in the system: HNO_3-HNO_2-H_2O-Np-1.09 *M*[3] tri-*n*-butyl phosphate in *n*-dodecane. A second objective was to determine the equilibrium constants for the oxidation reaction in the same system.

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[1] The information contained in this report was developed during the course of work under contract AT(07-2)-1 with the Atomic Energy Commission, whose permission to publish is gratefully acknowledged.

[2] G. T. Seaborg and J. J. Katz, "The Actinide Elements," National Nuclear Energy Series IV-14A, McGraw-Hill Book Co., New York, N. Y., 1954.

[3] Thirty volume per cent.