Structure of Acetylacetone by Electron Diffraction

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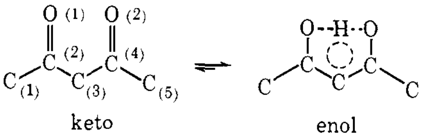
Abstract: A molecular structure investigation of the enol and keto tautomers of acetylacetone has been carried out by electron diffraction. It was found that the concentration of the enol form in the sample of the vapor at 105° was 66 ± 5%. The enol tautomer contains a short internal hydrogen bond, $O \cdots O = 2.381 \pm 0.020$ Å, which appears to be linear and symmetric. The hydrogen bond is part of a planar ring in which the bonded distances, $C–O = 1.315 \pm 0.007$ Å ($l_{C-O} = 0.041 \pm 0.004$ Å), $C–C = 1.416 \pm 0.010$ Å ($l_{C-C} = 0.035 \pm 0.006$ Å), are close to aromatic values. The other enol bonded distance is $C–C = 1.497 \pm 0.010$ Å ($l_{C-C} = 0.037 \pm 0.006$ Å). The ring angles are $OCC = 120.0 \pm 1.3°$ and $CCC = 118.0 \pm 2.5°$. The nonring angle is $CCC = 120.0 \pm 1.4°$. The keto tautomer is composed of two planar groups, each formed from the central carbon and an acetyl group, which are rotated with respect to each other through a dihedral angle of 48.6 ± 4°. In the keto form, the structural parameters are $C–O = 1.225 \pm 0.010$ Å ($l_{C-O} = 0.050 \pm 0.006$ Å) and $C–C = 1.540 \pm 0.015$ Å ($l_{C-C} = 0.070 \pm 0.008$ Å). The keto angles, denoting C_c as the central carbon atom, are $OCC_c = 120.0 \pm 1.8°$, $CC_cC = 114.0 \pm 3.6°$, and $CCC_c = 125.0 \pm 3.5°$. The $O \cdots O$ separation in the keto tautomer is 2.767 ± 0.030 Å. The distances are r_g values, and the errors are estimated to exceed the 95% confidence level.

Acetylacetone is a molecule with two tautomeric forms in dynamic equilibrium. The enol form is characterized by an internal hydrogen bond which



forms a stable six-membered ring and is the predominant form at room temperature.[1] Although many studies have been made of the equilibrium transition,[2] no direct structural studies have been made of the two forms of the molecule. The molecule is of particular interest because a crystal structure investigation by Schaefer and Wheatley[3] of tetraacetylethane, which is a dimer of the enol form of acetylacetone, had revealed that the intramolecular hydrogen bond is very short, 2.424 Å, and that the bonding in the ring had values implying aromatic character. It was of interest to determine if the stable ring configuration, with a small hydrogen bond, was preserved in the vapor phase. The ketone configuration could be expected to be very different from the enol form, with significant changes in bond lengths and orientation of the two acetyl groups. The 30 atoms comprising the two tautomeric forms produce 210 interatomic distances which contribute to the diffraction pattern. Among them, 80 distances are significantly distinct, presenting a complex challenge to the methods of electron diffraction analysis.

Experimental Procedure and Data Processing

Reagent grade acetylacetone was obtained from the Fisher Scientific Co. Its purity of better than 99.9% was confirmed by chromatographic analysis. The sample container and nozzle system were heated to the temperature range of 100–110° to provide adequate vapor pressure. A continuously monitored voltage at approximately 40 kV was recorded for each plate. A comparison wavelength calibration was performed with carbon disulfide. The sample to plate distance was measured for each plate and ranged in the vicinity of 110 mm. Kodak contrast emulsion projector slide plates were used for the photographs and were developed in nitrogen agitated Kodak Dektol solution.

The photographic plates were spun at about 300 rpm[4] and analyzed with scanning microdensitometers. The density data were read with both a Joyce Loebl Mark III densitometer and with a modified Leeds and Northrup densitometer. The output was recorded on tape in a form suitable for direct computer processing. The photographic densities were transformed to a total intensity function at intervals of 0.1 s units ($s = (4\pi \sin \theta/2)/\lambda$, where θ is the angle between the incident and scattered rays and λ is the electron wavelength). The data ranged from $3.05 \leq s \leq 31.55$ and were composed from five plates.

Analysis

The data reduction procedure[5] which transforms the total intensity curves into an experimental molecular intensity curve and a corresponding positive radial distribution function was facilitated by computer processing (see Appendix). The experimental,[6] calculated, and difference molecular intensity and radial distribution curves are given in Figures 1 and 2, respectively. The calculated curves are based on the models reported in Tables I and II, with the exception of the carbon–carbon distances C_1C_4 and C_2C_5 in the ketone structure, which exhibited an apparent shrinkage of 0.020 Å. In this investigation, the data reduction procedure was initiated by using the tetraacetylethane parameters[3] as a model for the enol. As the data reduction proceeded, an approximate model was developed for the keto form as well as a value for the relative composition by a study of the intensity and radial distribution functions of the tautomers. The final values of the parameters were

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[1] E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, p 376.

[2] L. W. Reeves, *Can. J. Chem.*, 35, 1551 (1957); J. Powling and H. J. Bernstein, *J. Amer. Chem. Soc.*, 73, 4353 (1951). For a more detailed discussion of the equilibrium, see ref 1.

[3] J. P. Schaefer and P. J. Wheatley, *J. Chem. Soc. A*, 528 (1966). This reference contains a list of several compounds with similarly short hydrogen bonds.

[4] I. L. Karle, D. Hoober, and J. Karle, *J. Chem. Phys.*, 15, 765 (1947).

[5] I. L. Karle and J. Karle, *ibid.*, 17, 1052 (1949); 18, 957, 963 (1950).

[6] A table of the molecular intensity data will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Reprint Department, ACS Publications, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

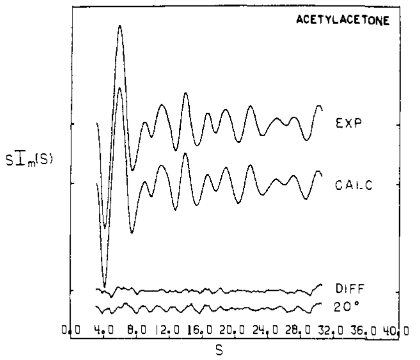

Figure 1. Experimental and calculated molecular intensity functions with difference curves. The difference curve labeled 20° indicates changes introduced into the intensity curve by rotating the methyl groups 20° from their reported orientations.

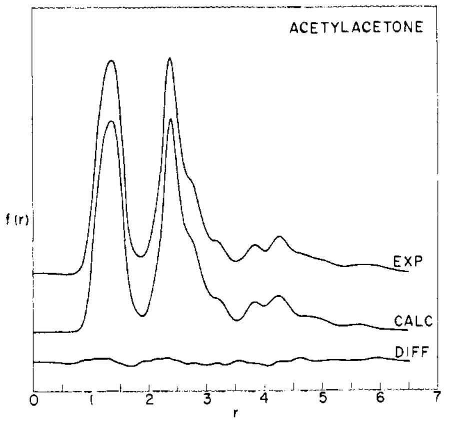

Figure 2. Experimental radial distribution function, calculated radial distribution function, and their difference. The damping factor, a in eq A4, was set equal to 0.003.

obtained from a least-squares procedure applied to the molecular intensity curve, whose values are constrained by the requirements that it be obtained from the total intensity functions by means of smooth background functions and that its Fourier transform be positive.

Table I. Coordinates Associated with r_a Distances[a] for the Enol Tautomer

	x	y	z
C(1)	−2.5219	0.0000	−0.0036
C(2)	−1.2132	0.0000	−0.7290
O(1)	−1.1903	0.0000	−2.0431
H(11)	−2.3358	0.0000	1.0826
H(12)	−3.0923	−0.9008	−0.2821
H(13)	−3.0923	0.9008	−0.2821
C(3)	0.0000	0.0000	0.0000
C(4)	2.5219	0.0000	−0.0036
C(5)	1.2132	0.0000	−0.7290
O(2)	1.1903	0.0000	−2.0431
H(51)	2.3358	0.0000	1.0826
H(52)	3.0923	0.9008	−0.2821
H(53)	3.0923	−0.9008	−0.2821
H(31)	0.0000	0.0000	1.1020
H	0.0000	0.0000	−1.9812

[a] In reference to this table and the next, the r_a distances are the parameters directly obtainable from the least-squares analysis. r_g values are the center of gravity positions associated with the probability functions and are related to the r_a values to a good approximation by $r_g = r_a + \langle l^2 \rangle / r_a$.

Table II. Coordinates Associated with r_a Distances for the Keto Tautomer

	x	y	z
C(1)	−2.6350	0.5851	−0.3823
C(2)	−1.2888	0.0000	−0.8370
O(1)	−1.2909	−0.4925	−1.9568
H(11)	−3.3807	0.4464	−1.1817
H(12)	−2.5123	1.6599	−0.1723
H(13)	−2.9684	0.0648	0.5301
C(3)	0.0000	0.0000	0.0000
C(4)	2.6350	−0.5851	−0.3823
C(5)	1.2888	0.0000	−0.8370
O(2)	1.2909	0.4925	−1.9568
H(51)	3.3807	−0.4464	−1.1817
H(52)	2.5123	−1.6599	−0.1723
H(53)	2.9684	−0.0648	0.5301
H(31)	0.0000	0.8764	0.6681
H(32)	0.0000	−0.8764	0.6681

The molecular intensity function for the least-squares analysis is given by

$$sI_m(s) = \sum_{i \neq j} \bar{g}_{ij} \exp(-\langle l_{ij}^2 \rangle s^2/2) \sin sr_{ij}/r_{ij} \qquad (1)$$

where $\bar{g}_{ij}$ is given by

$$\bar{g}_{ij} = \left[\frac{f_i(s) f_j(s)}{\sum_{k=1}^{N} [f_k^2(s) + S_k(s)/s^4]} \right]_{s_{\mathrm{exptl}}}$$

and $f_i(s)$ is the coherent atomic scattering factor for the ith atom in a molecule containing N atoms,[7] $S_k(s)$ is the incoherent scattering factor for the kth atom,[8] and the average over s extends over the range of experimental data. Because of the large number of distances which are nearly the same, the least-squares refinement was initiated using clustered distances. These clustered distances represented the contributions from both enol and keto distances which were grouped within 0.02–0.03 Å of each other, weighted according to their scattering power. The refined distances were used in a least-squares procedure for determining the coordinates of the two forms of the molecule, thus resolving the clustering into a "best" set of Euclidean distances and their associated atomic coordinates. The amplitude parameters from the clustered distances were used as starting parameters for further refinement on the vibrational amplitudes of the individual distances.

The validity of the least-squares analysis is associated with the possibility of resolving the radial distribution function, Figure 2. The radial distribution function is a superposition of the probability distribution functions associated with the interatomic distances occurring in the tautomers. It is resolvable into contributions from the component distances because of several constraints imposed on the system. They are: (a) the Gaussian shapes of the individual probability functions, (b) knowledge of the areas of the Gaussian functions in terms of the scattering factors, and (c) the important constraint imposed by the condition that the distribution of distances throughout the curve corresponds to chemically sensible structures

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[7] H. L. Cox, Jr., and R. A. Bonham, *J. Chem. Phys.*, 47, 2599 (1967).

[8] C. Tavard, D. Nicolas, and M. Rouault, *J. Chim. Phys. Physicochim. Biol.*, **64**, 540 (1967).

Table III. Structural Parameters Associated with the Enol and Keto Tautomers[a]

	Enol r_g	Enol $\langle l_{ij}^2\rangle^{1/2}$	Keto r_g	Keto $\langle l_{ij}^2\rangle^{1/2}$
C—H	1.109 ± 0.014	0.079 ± 0.008	1.109 ± 0.014	0.079 ± 0.008
C—O	1.315 ± 0.007	0.041 ± 0.004	1.225 ± 0.010	0.050 ± 0.006
C—C	1.416 ± 0.010	0.035 ± 0.006	1.540 ± 0.015	0.070 ± 0.008
C—C	1.497 ± 0.010	0.037 ± 0.006		
O···O	2.381 ± 0.020	0.057 ± 0.010	2.767 ± 0.030	0.110 ± 0.020
		Angles		
∠H(11)C(1)C(2)	109.3 ± 1.6		109.3 ± 1.7	
∠C(1)C(2)O(1)	120.0 ± 1.4		115.0 ± 1.8	
∠O(1)C(2)C(3)	120.0 ± 1.3		120.0 ± 1.8	
∠C(1)C(2)C(3)	120.0 ± 1.4		125.0 ± 3.5	
∠C(2)C(3)C(4)	118.0 ± 2.5		114.0 ± 3.6	
			Dihedral angle 48.6 ± 4.0	

[a] Bond lengths in ångströms, angles in degrees. The errors are limits of error above the 95% confidence level.

whose distribution of distances is definable to a close approximation by coordinates in a Euclidean system.

Results

The coordinates for the enol and keto models are given in Tables I and II, respectively. Principal structural parameters for the models are given in Table III and are shown in Figure 3. The errors given in Table III are above the 95% confidence level. Figure 4 shows the individual contributions of the enol and the keto forms to the calculated radial distribution function. The contribution of the two O···H distances of the internal hydrogen bond for the enol form is shown as well as the contributions from the bonded C—O and the O···O distances in both the enol and the keto forms. It was found that the enol tautomer possesses a planar ring having bonded distances typical of aromatic values and a small hydrogen bond with the O···O separation of 2.381 ± 0.020 Å. The keto assumes a configuration possessing two planar acetyl groups relatively rotated by a dihedral angle of 48.6 ± 4°. In the keto form, the O···O separation increases to 2.767 ± 0.030 Å. As can be seen in Figure 3, the enol form of the molecule has a methyl hydrogen atom trans to the near oxygen atom, while the keto form has the methyl hydrogen atom cis to the near oxygen atom. In order to test the sensitivity of this determination, a molecular intensity curve was calculated from a model in which the methyl hydrogen atoms were rotated 20° from their reported positions. In Figure 2, the curve labeled 20° shows the difference between the experimental intensity curve and the one from this model. It is seen that regular features of some significance appear in the difference curve, particularly in the range $8 \leq s \leq 16$, implying that, although the uncertainty in the orientation of the methyl groups is large, the intensity data are not insensitive to an arbitrary rotation of these groups.

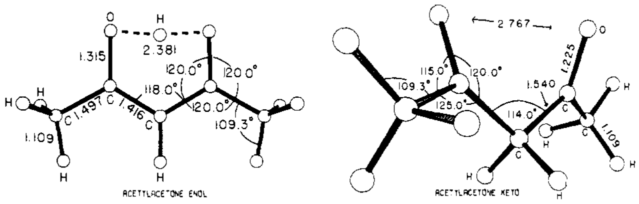

Figure 3. Structural parameters for the enol and keto tautomers.

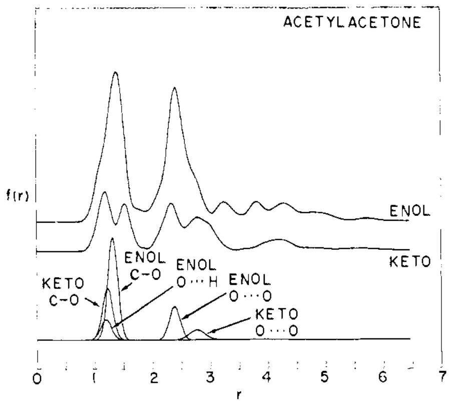

Figure 4. Partial decomposition of enol and keto contributions to calculated radial distribution function.

Discussion

There have been many investigations of the keto–enol equilibrium. Using nmr, Reeves[2] found approximately 65% of the enol form at 100° in the liquid phase. Using infrared band structure, Funck and Mecke[9] report approximately 90% of the enol at 100° in the gas phase. In this experiment, least-squares refinement on the scale parameters for the two forms of the molecule gives a concentration of the enol form of 66 ± 5% at an average sample temperature of ~105°.

A comparison of structural features with other molecules is given in Table IV. The small intramolec-

Table IV. A Comparison of Selected Distances in Several Molecules

	C—O	C—C	O···O
Acetylacetone (enol)	1.315	1.416[a] 1.497[b]	2.381
Acetylacetone (keto)	1.225	1.540	2.767
Acetone[c]	1.211	1.517	
Tetraacetylethane[d]	1.302	1.403[a] 1.489[b]	2.424
Acetic anhydride[e]	1.183[a] 1.405[b]	1.495	3.107

[a] Ring. [b] Chain. [c] Reference 10. [d] Reference 3. [e] Reference 12.

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[9] E. Funck and R. Mecke in "Hydrogen Bonding," D. Hadzi, Ed., Pergamon Press, London, 1959, p 433.

ular hydrogen bond distance of 2.424 Å, observed by Schaefer and Wheatley[3] for the crystal of tetraacetylethane (TAE), compares with the somewhat smaller value of 2.381 Å for acetylacetone (AA). The C–O bonded distance in TAE is 1.302 Å compared with the 1.315-Å distance in the enol form of AA. The bonded C–C distance in the ring of TAE is 1.403 Å compared with 1.416 Å in AA, and the methyl C–C bonded distance in TAE is 1.489 Å compared with 1.497 Å in AA. The structural parameters for the keto form of acetylacetone may be compared with the parameters from a recent investigation of acetone by Kato, *et al.*[10] They found a C=O bonded distance of 1.211 Å in acetone with which the keto C=O bonded distance of 1.225 Å may be compared. The C–C bonded distance in acetone is 1.517 Å compared with the 1.540-Å distance in AA. It is of interest to note that in heavy metal acetylacetonate structures, where a heavy metal atom replaces the hydrogen atom of the internal hydrogen bond, intramolecular O···O distances range in the vicinity of 2.8 Å,[11] while the carbon–oxygen ring structure remains planar and the bond distances in the ring are typical of aromatic systems. A structure similar to the keto tautomer is that of acetic anhydride. Vledder, *et al.*,[12] report two planar acetyl groups, connected, in this case, to a central oxygen atom and rotated relative to each other by a dihedral angle of 78.8°. For the anhydride, the C=O and C—C bonds are reported to be smaller, C=O = 1.183 ± 0.007 Å and C—C = 1.495 ± 0.002 Å. Designating C_c as the central carbon atom in acetylacetone, corresponding to the central oxygen in the anhydride, O_c, the angle which corresponds to the angle CCC_c in the keto tautomer is considerably smaller, $\angle CCO_c = 108.3°$. The angle corresponding to the angle CC_cC in the keto form is closer in value, $\angle CO_cC = 115.8°$.

In acetylacetone, the internal hydrogen bond appears to be linear and symmetric. This conclusion is based on the good fit to the experimental data provided by the two O···H distances at 1.19 Å. The contribution of these distances to the left side of the peak at 1.3 Å, corresponding to bonded distances, may be seen in Figure 4. Reported values for O–H bond lengths, in nonsymmetrical hydrogen bonds, range around 1.0 Å.[13] This value produces O—H and H···O distances which are not consistent with our experimental radial distribution curve. In a recent investigation of hexafluoroacetylacetone, Andreassen, *et al.*,[14] reported a similar type of hydrogen bond at 2.551 ± 0.033 Å. Ogoshi and Nakamoto[15] reported a normal-coordinate analysis of both acetylacetone and the hexafluoro analog. They based their calculations on a structure with parameters similar to dibenzoylmethane and assumed a bent hydrogen bond. With an O···O separation of 2.5 Å, the normal-coordinate analysis yielded force constants of 4.0 mdyn/Å for O—H and 0.3 mdyn/Å for H···O. Similar results were obtained for the hexafluoroacetylacetone. In an earlier calculation involving linear intermolecular hydrogen bonds, Nakamoto, *et al.*,[16] predicted that as the O···O distance became smaller, the O—H and H···O stretching force constants would approach each other in magnitude. For the distance of 2.5 Å, which they assumed for the acetylacetone, they expected the force constants to be 2.0 and 1.0 mdyn/Å, respectively.[15] These values should be compared with the values from the bent-bond calculation above. Since both electron diffraction studies indicate a linear symmetrical hydrogen bond, it is possible that the internal hydrogen bonds of this small size do reflect the behavior predicted by the calculations on linear intermolecular hydrogen bonds.

Appendix

Weighted averages of functions of the form

$$b_p(s) = \exp(\alpha_p + \beta_p s^{\gamma_p}) \qquad \text{(A1)}$$

are employed to obtain smooth background functions which generate from the total intensity functions a molecular intensity function whose Fourier transform is essentially positive. The process for generating the background functions begins by using eq A1 to fit sets of points in several overlapping segments (labeled with p) ranging over the experimental values of s. The s range of each segment is made to partially overlap the s range of adjacent segments. These sets of points may be obtained at first from the null points corresponding to those of a theoretical molecular intensity function computed from an initial model of the structure. As the process continues, the points are obtained from the use of the Fourier inversion of "positivized" radial distribution functions or from structure models obtained from the improved experimental intensity functions as described below.

The constants α_p, β_p, and γ_p for each background function $b_p(s)$ are calculated either by solving three simultaneous equations for three points or by a least-squares procedure to fit a larger set of background points in the appropriate s range. The composite background intensity function, $I_b(s)$, is a weighted sum of the contributions from the individual functions $b_p(s), p = 1, \ldots, m$, composed in the following way.

A partial weighted sum may be defined by

$$B_p(s) = u_p(s)B_{p-1}(s) + v_p(s)b_p(s),\ p = 1, \ldots, m \qquad \text{(A2)}$$

where $B_0(s) = 0$, $B_1(s) = b_1(s)$, and the coefficients $u_p(s)$ and $v_p(s)$ are weighting functions in the region of s where $B_{p-1}(s)$ and $b_p(s)$ overlap. The coefficients form a smooth joining of the functions and have the following properties. (a) For values of s less than the defined region of $b_p(s)$, $u_p(s) = 1$ and $v_p(s) = 0$. (b) In the region of s where $B_{p-1}(s)$ and $b_p(s)$ overlap, $u_p(s)$ varies linearly from 1 to 0 and $v_p(s)$ varies linearly from 0 to 1 such that $u_p(s) + v_p(s) = 1$. (c) For values of s larger than the defined region for $B_{p-1}(s)$, $u_p(s) = 0$ and $v_p(s) = 1$. Equations A2 represent a

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(10) C. Kato, S. Konaka, J. Ijima, and M. Kimura, *Bull. Chem. Soc. Jap.*, **42**, 2148 (1969).

(11) B. Morosin and J. R. Brathovde, *Acta Crystallogr.*, 17, 705 (1964), report an average O···O distance between oxgen atoms of the same acetylacetone moiety of 2.805 Å for tris(acetylacetonato)manganese-(III); B. Morosin, *ibid.*, 19, 131 (1965), reports an average O···O distance of 2.786 Å for tris(acetylacetonato)chromium.

(12) H. J. Vledder, F. C. Mijlhoff, J. C. Leyte, and C. Romers, *J. Mol. Struct.*, 7, 421 (1971).

(13) J. Donohue in "Structural Chemistry and Molecular Biology," A. Rich and N. Davidson, Ed., W. H. Freeman, San Francisco, Calif., 1968; W. Hamilton and J. Ibers, "Hydrogen Bonding in Solids," W. A. Benjamin, New York, N. Y., 1968.

(14) A. L. Andreassen, D. Zebelman, and S. H. Bauer, unpublished results.

(15) H. Ogoshi and K. Nakamoto, *J. Chem. Phys.*, **45**, 3113 (1966).

(16) K. Nakamoto, V. A. Sarma, and H. Ogoshi, *ibid.*, **43**, 1177 (1965).

stepwise process for constructing the background intensity function, $B_n(s) \simeq I_b(s)$ in n steps.

An initial smooth background line is obtained by using null points from a molecular intensity function computed from a model of the structure and fitting the functions $b_p(s)$ to a sequence of segments, each containing three points of the total intensity curve coincident with alternate null points. The molecular intensity function $I_m(s)$ is obtained in the usual manner from the total intensity function $I_t(s)$ using[5]

$$I_m(s) = (I_t(s)/I_b(s)) - 1 \qquad \text{(A3)}$$

The radial distribution function f(r)

$$f(r) = (2/\pi)^{1/2}\int_0^{s_{max}} sI_m(s)\exp(-as^2)\sin srds \qquad \text{(A4)}$$

is made positive by attaching "Gaussian tails" to the edges of the significant nonzero peaks. A Gaussian function is fitted by least squares to the lower 5–10% of the peak edge. The function is then smoothly averaged with the lower 2–5% of the peak edge and used as the extension of the peak in the region where it should have small values. The entire radial distribution function is made positive in this manner and then transformed to yield the next approximate molecular intensity function, which is used to generate new points for an improved background intensity function. The improved $I_b(s)$ is obtained from eq A3 using the $I_m(s)$ obtained from the "positivized" radial distribution curve. Many values of the new $I_b(s)$ may now be employed with a least-squares calculation to fit the functions $b_p(s)$, eq A1, to $I_b(s)$ in several overlapping ranges of s. A new composite background intensity function is then derived from the process described by eq A2. Further recycling ultimately produces a smooth background intensity function $I_b(s)$ which generates an essentially positive radial distribution curve obeying the area criterion.[5]

Studies of Some Aspects of Solution Character by Molecular Spectroscopy. IV. On the Multiplicity and Nature of the $Co(CO)_4^-$ Environments in Certain Solvents[1,2]

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Abstract: The infrared band near 1900 cm^{-1} was examined for $NaCo(CO)_4$ in eight solvent systems. The band envelope was found to be simple for DMF, DMSO, and wet THF, but showed varying degrees of complexity for pyridine, piperidine, THF, and DME. Water is sufficiently different to be considered a special case. The results are discussed in terms of the differing multiplicities and differing nature of the anion environment. A band component near 1887 cm^{-1} is found in all solutions but water (and perhaps piperidine), and it is associated with the internal vibration of the anion in a symmetrical "solvent-surrounded" ion environment. Band components above and below this frequency are associated with the anion in asymmetrical solution environments.

The discovery that alkali ions vibrate in solution offers an opportunity to investigate the dynamics, forces, and structure in solutions near ions.[1b] A more complete understanding of the vibration of an alkali ion is obtained if one has an understanding of its immediate surrounding in the solution. It has been found that a single broad infrared band is observed for this vibration in virtually all of the solutions examined to date.[1b,c,4-8] These cases cover a variety of salts and solvents. Does this mean that the alkali ion is found in only one environment in these solutions? This question is investigated in this study.

The intramolecular vibrations of a polyatomic ion reflect its immediate surroundings. Hence, the internal vibrations of a polyatomic anion in solution serve as a probe of the anion environment and, *mutatis mutandis*, of that of the cation. The tetracarbonylcobaltate ion, $Co(CO)_4^-$, was chosen as an anionic probe of the ion environments for this study because its salts are soluble in a variety of solvents. Moreover, the C–O stretching frequencies near 1900 cm^{-1} are sensitive to environment. The solvents chosen cover a wide range of solution properties, while the differences between Li^+, Na^+, and K^+ salts were examined in a single solvent of intermediate character.

Experimental Section

The infrared measurements were made in the 1900-cm^{-1} region with a Perkin-Elmer spectrophotometer, Model 421. Cells with CaF_2 or KBr windows were used. The solvents used in this study

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[1] (a) Part I: W. F. Edgell, M. T. Yang, and M. Koizumi, *J. Amer. Chem. Soc.*, 87, 2563 (1965). (b) Part II: W. F. Edgell and A. T. Watts, Abstracts, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1965, p 85; W. F. Edgell, A. T. Watts, J. Lyford, IV, and W. Risen, Jr., *J. Amer. Chem. Soc.*, 88, 1815 (1966). (c) Part III: W. F. Edgell, J. Lyford, IV, R. Wright, W. Risen, Jr., and A. T. Watts, *ibid.*, 92, 2240 (1970).

[2] Based in part upon the Ph.D. theses of J. Lyford, IV, June 1969, and of A. Barbetta, in preparation.

[3] On leave from the National Chemical Laboratory, Poona, India.

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