

Crystal and Molecular Structure of Biacetyl (2,3-Butanedione), (H₃CCO)₂, at -12 and -100 °C

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Abstract: The crystal structure of solid biacetyl has been determined at -12 and -100 °C. Crystals are monoclinic, space group $P2_1/n$, with unit cell parameters $a = 7.514$ (29) Å, $b = 5.249$ (22) Å, $c = 6.552$ (21) Å, and $\beta = 116.1$ (3)° at -12 °C and $a = 7.384$ (35) Å, $b = 5.205$ (27) Å, $c = 6.533$ (28) Å, and $\beta = 117.4$ (4)° at -100 °C, $Z = 2$, $d(\text{calcd}) = 1.232$ g cm⁻³ at -12 °C, $d(\text{calcd}) = 1.280$ g cm⁻³ at -100 °C. Data were collected on a Nicolet P2₁ diffractometer and refined by least-squares methods to $R = 0.048$ at -12 °C and $R = 0.081$ at -100 °C. There is no phase transition between -12 and -100 °C. The biacetyl molecule has the trans configuration and molecular symmetry $\bar{1}$. The most important distances are C=O = 1.209 (6) Å, C—C(methyl) = 1.476 (6) Å, and C—C(central) = 1.540 (6) Å. The high value for the central C—C distance is discussed. The six non-hydrogen atoms are coplanar.

For the interpretation of spectroscopic and EPR data obtained from crystalline biacetyl, H₃CCOC(=O)CH₃, at 1.2 K,² it was necessary to have precise structural information for these crystals, specifically about (a) the planarity of the molecule, (b) the orientation of the molecules in the solid with respect to the crystallographic axes, and (c) the C=O and central C—C bond distances. Furthermore the molecule has a conjugated system of double bonds analogous to that of butadiene, which has a short central C—C bond. Yet molecules in which the C=CH₂ of butadiene is replaced by C=O do not show a similar shortening of the central C—C bond. Notable examples are oxalic acid and many of its derivatives. The structure determination of crystalline biacetyl was undertaken for these reasons.

Experimental Section

The title compound was purchased from Matheson, Coleman and Bell and purified by repeated vacuum distillation, eventually yielding a light yellow liquid at room temperature. A small amount of liquid was distilled into a thin-walled Pyrex capillary, of 0.5-mm diameter, which was then mounted on a Nicolet P2₁ automated diffractometer equipped with a low-temperature (LT) unit. The LT unit provides a stream of nitrogen gas, cooled by liquid nitrogen, which is aimed directly at the crystal. The temperature of the gas stream can be controlled. We succeeded in growing a single crystal of the compound in situ, by carefully regulating the gas temperature around the melting point of -3 °C. After the crystal was formed the gas temperature was lowered to -12 °C and a set of intensity data was collected. Subsequently the temperature was decreased to -100 °C and a second data set was collected at the lower temperature, in order to determine (a) the unit cell parameters at both temperatures and (b) whether or not any phase change occurred between the two temperatures. Crystal data for both temperatures are reported in Table I. Temperatures are accurate to within ± 2 °C.

Intensity data were collected using Mo K α radiation ($\lambda = 0.71069$ Å) and a graphite monochromator. The range of 2θ was 0–50°, the minimum scan rate was 2°/min, and the background/scan time ratio was 0.5. The data set at -100 °C was considerably inferior in quality to that at -12 °C, due to crystal strain, cracking of the crystal, and icing problems at the lower temperature. A total of 416 independent reflections (including 63 with intensity $< 3\sigma(I)$) were measured at -12 °C, and 320 reflections (including 79 with $I < 3\sigma(I)$) at -100 °C.

Intensities were corrected for Lorentz and polarization factors. No absorption correction was applied, because (a) all atoms are light and their absorption of Mo K radiation is very low and (b) the size of the crystal was not known with any accuracy. The structure from the -12 °C data was worked out first. The positions of the non-hydrogen atoms could be determined directly from a Patterson map, and these positions were refined by least-squares methods. At further stages of the refinement the hydrogen atoms were included and in the final stages the refinement involved positional parameters for all six independent atoms, anisotropic thermal parameters for the non-hydrogen atoms, isotropic thermal parameters for the three hydrogens, and a scale factor. The final

Table I. Crystal Data for Biacetyl

	-12 °C	-100 °C
space group	$P2_1/n$	$P2_1/n$
a , Å	7.514 (29)	7.394 (35)
b , Å	5.249 (22)	5.205 (27)
c , Å	6.552 (21)	6.533 (28)
β , deg	116.1 (3)	117.4 (4)
Z	2	2
$d(\text{calcd})$, g cm ⁻³	1.232	1.280
V , Å ³	232.0	223.2

values for the discrepancy indices were $R = 0.048$ and $R_w = 0.066$.³ The final value of the goodness-of-fit was 2.034.

In order to determine the structure at -100 °C the parameters for the high temperatures were taken as starting values and these were refined by least squares to a final value of $R = 0.081$ and $R_w = 0.094$.³ Table II gives the final atomic parameters and Table III gives the most important interatomic distances and angles in the molecule, calculated for the -12 °C parameters, which are the more reliable of the two sets. Distances at -100 °C are within 1 standard deviation from those at -12 °C. Figure 1 shows a stereo view of the unit cell. Tables of F_o and F_c at both temperatures are available.⁴

Discussion

The structure does not change significantly between the two temperatures, except for (a) a significant decrease of the thermal motion parameters at the lower temperature and (b) the expected contraction of the cell parameters with decrease in temperature. The largest contraction is for the a axis (1.6%). There is no phase transition between -12 and -100 °C. The six non-hydrogen atoms in the molecule are all coplanar, in agreement with the fact that the molecule has a pair of conjugated double bonds. The planes in which the molecules lie are (110) and (1 $\bar{1}$ 0). Calculation of the least-squares plane through these six atoms shows that the largest deviation from the plane is only 0.003 Å, for C(1), and that H(2) lies fairly close to this plane, at 0.12 Å distance. Since the molecule is located across a center of inversion the oxygen atoms are trans to one another, as are the methyl groups.

The interatomic angles agree with sp² hybridization of the central carbon atoms C(1) and C(1)' combined with a weak repulsion between oxygen and the methyl group. The most noteworthy feature of the structure is the long distance of 1.540 Å between C(1) and C(1)' across the inversion center. If the molecule contained a conjugated system of double bonds, this distance would be expected to be considerably shorter, close to the values of 1.483 Å found for buta-1,3-diene⁵ and 1.45 Å for

(3) $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; $R_w = (\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2)^{1/2}$.

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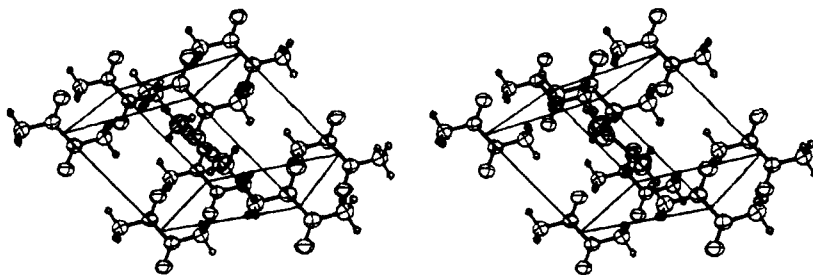


Figure 1. Stereoview of the unit cell of biacetyl.

Table II. Atomic Parameters for Structure^a

atom	x	y	z	U_{11}/U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	
-12 °C										
O	0.0921 (2)	0.1804 (2)	0.2438 (2)	8.56 (9)	5.65 (9)	5.38 (8)	-1.32 (7)	2.88 (7)	-1.58 (6)	
C(1)	-0.0023 (2)	0.0120 (3)	0.1160 (2)	5.24 (7)	4.36 (9)	4.68 (9)	0.52 (8)	1.76 (7)	-0.24 (8)	
C(2)	-0.1254 (4)	-0.1743 (5)	0.1651 (4)	6.94 (12)	6.65 (15)	5.77 (12)	-0.86 (10)	3.11 (10)	-0.65 (10)	
H(1)	-0.092 (4)	-0.338 (6)	0.137 (4)	7.9 (7)						
H(2)	-0.102 (4)	-0.154 (4)	0.321 (5)	7.5 (6)						
H(3)	-0.254 (4)	-0.143 (4)	0.067 (5)	7.7 (7)						
-100 °C										
O	0.0953 (7)	0.1842 (5)	0.2475 (4)	6.71 (33)	2.83 (20)	3.80 (21)	-0.65 (19)	2.53 (21)	-0.81 (11)	
C(1)	-0.0029 (9)	0.0149 (8)	0.1155 (7)	4.33 (33)	2.20 (22)	3.51 (24)	0.35 (24)	1.91 (24)	0.11 (15)	
C(2)	-0.1318 (12)	-0.1693 (10)	0.1606 (10)	5.87 (42)	3.30 (28)	4.06 (29)	-0.62 (30)	2.74 (29)	-0.30 (18)	
H(1)	-0.088 (15)	-0.349 (16)	0.138 (11)	7.6 (2.3)						
H(2)	-0.108 (11)	-0.155 (9)	0.320 (9)	4.2 (1.4)						
H(3)	-0.290 (18)	-0.126 (17)	0.050 (14)	10.2 (3.0)						

^a Thermal parameters, U_{ij} and U , have dimensions Å². The form of the anisotropic temperature factor is $\exp[-2\pi^2 \sum_{ij} h_i h_j a_i^* a_j^* U_{ij}]$. Values of U_{ij} and U have been multiplied by 100.

Table III. Interatomic Distances (Å) and Angles (deg)^a

C(1)-O	1.209 (6)	C(2)-C(1)-C(1)'	116.7 (2)
C(1)-C(2)	1.476 (6)	C(1)-C(2)-H(1)	108 (2)
C(1)-C(1)'	1.540 (6)	C(1)-C(2)-H(2)	109 (2)
C(2)-H(1)	0.94 (3)	C(1)-C(2)-H(3)	108 (2)
C(2)-H(2)	0.97 (4)	H(1)-C(2)-H(2)	112 (2)
C(2)-H(3)	0.91 (3)	H(1)-C(2)-H(3)	109 (2)
O-C(1)-C(2)	124.5 (3)	H(2)-C(2)-H(3)	111 (3)
O-C(1)-C(1)'	118.8 (2)		

^a C(1) and C(1)' denote the central carbon atoms related by the center of inversion. C(2) is the methyl carbon atom.

propenal.⁶ In molecules O=C(R)-C(R)=O, however, the central C-C bond length is always found to be much longer, as demonstrated in Table IV. This deviation must be a consequence of the high electronegativity of oxygen, and it can be understood if one accepts that the resonance structure O⁻C⁺(R)C⁺(R)O⁻ contributes significantly to the electron distribution in these oxygen-containing conjugated molecules. In this resonance structure the central C-C bond is single, and the carbon atoms both have a formal positive charge. The analogous resonance structure in butadiene cannot have significant importance since in the case the terminal atoms are carbon and there will be little or no tendency for these to attract electrons and thereby assume a formal negative charge. This assumption is supported by MO calculations for the oxalate ion¹³ and for biacetyl,¹⁴ which come to the correct conclusion that the central C-C bond length should be long, and close to 1.54 Å.

The bond distance of 1.476 Å for C(1)-C(2), where C(2) = C(methyl), is close to the distance that can be expected for the

Table IV. Bond Lengths in O=C(R)-C(R)=O Molecules^a

compound	R	C-C, Å		ref
		C-C, Å	C=O, Å	
biacetyl	CH ₃	1.540	1.209	this work
oxalic acid	OH	1.537	1.222, 1.207	7
oxalate ion	O ⁻	1.561	1.252, 1.264	8
oxamide	NH ₂	1.542	1.243	9
oxalyl bromide	Br	1.56	1.17	10
dimethyl oxalate	OCH ₃	1.53	1.19	11
hydrogen oxalate ion	OH, O ⁻	1.549	1.236, 1.204	12

overlap between a carbon sp² and a carbon sp³ orbital. Listings of such interactions (see ref 15) show values around 1.50-1.51 Å. In the closely related molecule dimethylglyoxime¹⁶ the C-C-(methyl) distance is 1.479 Å, while in several metal-dimethylglyoximes it is found to be 1.44 Å,¹⁷ 1.46 Å,¹⁸ and 1.50-1.53 Å.¹⁹ It is worth noting that similar C(sp²)-C(sp³) bond lengths determined by gas electron diffraction (ED) or microwave (M) methods are found to be somewhat longer. Examples are 1.501 Å in acetaldehyde(M),²⁰ 1.506 Å in propene (ED),²¹ 1.488 Å in propene (M),²² 1.505 Å in acetyl chloride (ED)²³ and 1.505 Å in acetyl fluoride (ED).²⁴ Measurements of distances by X-ray diffraction, particularly in small molecules that exhibit considerable thermal vibration, tend to be foreshortened as a result of the vibrational motion of the atoms.²⁵ The bond length for C(1)-C(2) reported here is not in disagreement with values found by use of other methods.

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The structure of gaseous biacetyl was determined, at 225 and 525 °C, by using gas electron diffraction.²⁶ The results agree with those reported here: (1) the configuration of the gaseous molecule is only trans; (2) the C=O bond distance (1.215 Å) is within one standard deviation from the value found by us in the solid; (3) the central C—C distance is found to be longer than the C—C(methyl) distance, by 0.014 Å at 225 °C and by 0.028

Å at 525 °C. In the structure of the solid the difference is 0.064 Å, but again, as pointed out above, the foreshortening of the C—C(methyl) distance in the solid may tend to exaggerate this difference.

Registry No. 2,3-Butanedione, 431-03-8.

Supplementary Material Available: Tables 5 and 6 listing F_o and F_c at both temperatures (7 pages). Ordering information is given on any current masthead page.

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An Experimental and ab Initio Study of the Addition of Atomic Carbon to Water

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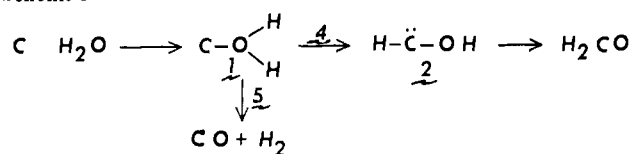
Abstract: Experimental and theoretical investigations of the reaction of atomic carbon with H₂O were carried out and the results compared. The theoretical study, in which all geometries were optimized at 3-21G level and single point calculations performed at the UMP3/6-31G** level, involved both ¹D and ³P states of carbon. For C(¹D) atoms, the process having the lowest activation enthalpy is cleavage of an initially formed carbon-water complex to CO and H₂ along a closed-shell surface ($\Delta H^\ddagger = 5.2$ kcal/mol). Rearrangement of the closed-shell carbon-water complex to hydroxymethylene has $\Delta H^\ddagger = 11.6$ kcal/mol. In the case of triplet carbon, the most favorable reaction of the initial carbon-water complex was simply dissociation to C + H₂O. The ΔH^\ddagger for rearrangement of the C(³P)-H₂O complex to hydroxymethylene was 22.8 kcal/mol while the corresponding barrier for an open-shell singlet complex was 18.0 kcal/mol. The barrier to rearrangement of singlet hydroxymethylene to formaldehyde (38.9 kcal/mol) and that of triplet hydroxymethylene (41.3 kcal/mol) were similar. The experimental results were in agreement with theoretical predictions. Atomic carbon, generated by the thermolysis of 5-diazotetrazole, reacts with water to give carbon monoxide (9.5%) and formaldehyde (2.4%). Addition of O₂, a scavenger of C(³P), increases the CO yield to 53.7% while leaving the formaldehyde yield unchanged. Reaction of carbon with O₂ alone produces only CO (47%). These results indicate that the state of carbon reactive toward water is a singlet, as indicated by the calculations.

Over the past several years it has become possible to apply ab initio methods to the study of potential energy surfaces with the thoroughness heretofore reserved for semiempirical methods. In particular, it is now feasible to obtain accurate ab initio predictions of reaction mechanisms and compare these predictions with experimentally observed pathways. In this paper we have utilized this approach to investigate the reaction between atomic carbon and water both experimentally and theoretically.

A study of the rather simple reaction of carbon with water is advantageous from both an experimental and a theoretical viewpoint. The fact that there are only four atoms involved in this system reduces the time required for computations and limits the number of product-forming steps that the experimentalist need consider.

Since there is little doubt that initial attack of carbon on water will occur at oxygen, we may formulate the pathways shown in Scheme I.¹ Both deoxygenation (via transition state 5) and O-H insertion (via transition state 4) have been observed in the reaction of carbon atoms with alcohols.² This paper will describe the energetics of the formation and subsequent reactions of the carbon-water complex, 1, the effect of the electronic state of carbon on the reaction, and the relative contributions of the reaction pathways in Scheme I.

Scheme I



Previous reports of the use of MO methods to study the reactions of atomic carbon have been limited to reactions with hydrogen,³ ethylene,⁴ oxirane,⁵ and carbonyl compounds.⁶

Method of Calculation

All stationary points have been located by using the GAUSSIAN80 program package⁷ with no constraints except for symmetry when appropriate. The 3-21G basis set,⁸ which has been shown to give results nearly identical with larger basis sets, is used to determine geometries. The geometries have been optimized by using analytical derivatives, and transition states have been located by finding a stationary point that has a developing negative eigenvalue

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