Complexes of Ketones with SbF_5 in the Condensed Phase. Structural Effects on the Carbonyl Stretching Frequencies

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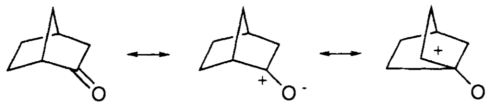
The cryochemical matrix isolation method has been used to measure the down frequency shift of C=O stretching vibrations ($\Delta\nu$) which originate from ketones complexing with SbF_5. Such ketone–SbF_5 complexes can serve as good models of analogous carbocations. The weakening of the C=O bond in the complex is a consequence of its increased polarization. The influence of the hydrocarbon skeleton on the stabilization of the incipient positively charged carbon atom is qualitatively similar to that in carbocations. Examined ketones **1–23** can be sorted into two categories. Complexes of ketones similar to classical carbocations belong to the first category. Because in this group the inductive donation of electrons to the positively charged carbon atom is the dominant effect, the $\Delta\nu$ values correlate well with the number of C_α–C_β bonds. Ketone complexes in which the $\Delta\nu$ values substantially deviate from the linear correlation belong to the second category where the structures of the hydrocarbon skeleton are the same as in carbocations in which other stabilizing effects are operative. The observed deviation from linearity can be rationalized by other effects such as hyperconjugation, bridging, participation and homoaromaticity. This view has been supported by semiempirical and *ab initio* calculations.

Addition reactions to the trigonal carbon atom are at the heart of solvolytic processes proceeding *via* cationic intermediates and also of reactions of the carbonyl group. The pioneering work of Dunitz and Burgi,[1a] Kirby[1b] and others demonstrated the correlation of ground state crystal structures of ketones with reactivity and stereoselectivity of nucleophilic addition reactions to the carbonyl group. On the other hand, almost 30 years ago Foote[2] and Schleyer[3] quantitatively correlated carbonyl stretching frequencies of ketones with the solvolytic reactivity of corresponding arenesulfonates. Also, it has been shown that the ionization energies of aldehydes and ketones correlate well with the inductive substituent constants $\Sigma\sigma_I$ of the corresponding alkyl groups.[4] Hyperconjugation of antiperiplanar σ-bonds involving delocalization into incipient σ* orbitals was offered by Cieplak[5] and le Noble[6] as an explanation of the preferred face selection in addition reactions of nucleophiles to the carbonyl group. This is in fact an extension of Winstein's original proposal[7] of σ participation being responsible for retention of configuration in some solvolyses. Recently, it has been shown that electronic interactions commonly observed in carbocations can also be observed in ketones if they are complexed with strong Lewis acids which increases by polarization the carbocation character of the carbonyl group.[8] Such complexes were studied in detail by ^1H, ^{19}F and ^{13}C NMR spectroscopy. Laube[9] determined the crystal structure of the complex 5-phenyladamantan-2-one–pentachloroantimony and two 3,3,5,5,-tetraalkylcyclohexanones activated by Li^+ and $SbCl_5$, and in all cases found a lengthening of the C=O bond, while the bonds to the α-carbons were shortened and C_α–C_β bonds lengthened again. A similar elongation of the C=O bond has been obtained by *ab initio* calculation of complexes of aldehydes and ketones with H^+ and various neutral Lewis acids.[10] Childs *et al.*[11] have shown that protonated cyclopropyl ketones adopt in the crystal as hexafluoroantimonate salts a conformation which is consistent with the one expected for a bisected cyclopropylcarbinyl cation. Hyperconjugation and σ participation were considered to be important factors for these structural changes. Support for this reasoning also comes from low-temperature ^{13}C NMR spectra of carbocations and ketone complexes with Lewis acids.[12]

In continuation of our work on low-temperature IR spectroscopy of carbocations in antimony pentafluoride matrices[13] we considered it of interest to study the vibrational spectra of a series of SbF_5 complexes of ketones which are structurally related to previously well studied carbocations. This may have the additional advantage in cases where spectra of the corresponding carbocations cannot be observed directly because of rapid rearrangements to more stable ions as is the case with the cyclohexyl cation.[14] Specifically we were interested in changes in the carbonyl stretching frequencies $\Delta\nu$ of the complexed ketones in comparison with the C=O frequencies of the parent ketones.

$$\Delta\nu = \nu_{C=O}(\text{ketone}) - \nu_{C=O}(\text{complex})$$

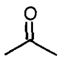
These changes should reflect the enhanced carbocation character of the carbonyl group due to a greater contribution of the dipolar resonance structure as exemplified for norbornan-2-one. For the purpose of the present investigation, ketones **1–23**



were chosen on the basis of the following two criteria. The first one was topological, based on the number of α–β C–C bonds N, related supposedly to the inductive effect of these bonds. For the second criterion, ketones were selected to be structurally analogous to carbocations additionally stabilized by other manifolds (hyperconjugation, σ-participation, *etc*). In order to additionally clarify the contribution of these effects on structure and on vibrational changes, semiempirical and *ab initio* calculations were performed on protonated, BF_3 and SbF_5 complexes of some simple aldehydes and ketones.

Methods and Materials

The required ketones were commercial products of the highest grade and were used without further purification. Compounds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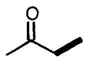
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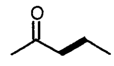
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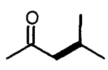
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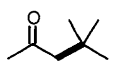
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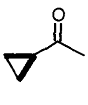
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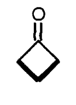
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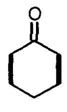
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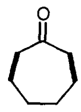
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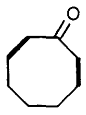
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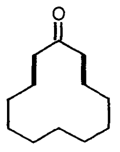
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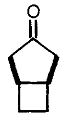
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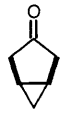
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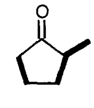
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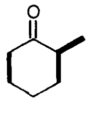
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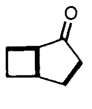
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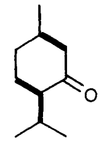
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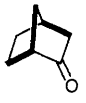
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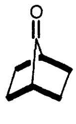
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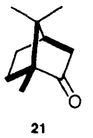
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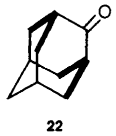
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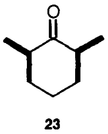
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Table 1 Experimental C=O stretching frequencies (ν/cm^{-1}) of ketones **1**–**23** and corresponding SbF_5 complexes

Ketone	N	$\nu_{C=O}$	$\nu_{C=O\text{-}SbF_5}$	$\Delta\nu$
1 Acetone	0	1700	1590	110
2 Butan-2-one	1	1705	1585	120
3 Pentan-2-one	1	1718	1597	121
4 4-Methylpentan-2-one	1	1714	1586	128
5 4,4-Dimethylpentan-2-one	1	1717	1566	151
6 Cyclopropyl methyl ketone	2	1685	1525	160
7 Cyclobutanone	2	1765	1615	150
8 Cyclopentanone	2	1735	1610	125
9 Cyclohexanone	2	1705	1580	125
10 Cycloheptanone	2	1690	1565	125
11 Cyclooctanone	2	1690	1530	160
12 Cyclododecanone	2	1690	1560	130
13 Bicyclo[3.2.0]heptan-3-one	2	1737	1567	170
14 Bicyclo[3.1.0]hexan-3-one	2	1741	1556	185
15 2-Methylcyclopentanone	3	1725	1590	135
16 2-Methylcyclohexanone	3	1708	1535	173
17 Bicyclo[3.2.0]heptan-2-one	3	1730	1570	160
18 Menthone	3	1700	1531	169
19 Norbornan-2-one	3	1745	1570	175
20 Norbornan-7-one	4	1780	1610	170
21 Camphor	4	1730	1540	190
22 Adamantanone	4	1715	1550	165
23 2,6-Dimethylcyclohexanone	4	1705	1534	171

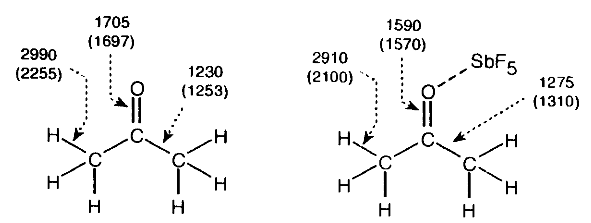
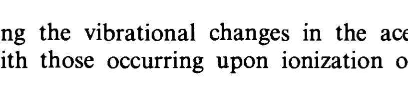


Fig. 1 Vibrational frequencies of acetone and acetone–SbF_5 complex (in cm^{-1}). The numbers in parentheses are the vibrational frequencies for hexadeuteriated compounds.

13–**15**, **17** and **20**, were prepared following the published procedures.[15–17] The matrix deposition on the CsI window at 77 K was performed by applying the previously described technique.[13] Spectra were taken on a Perkin-Elmer Spectrometer Model 167 or 1725X (FT) and recorded repeatedly while warming the matrix to 200 K. Semiempirical calculations (AM1 and PM3) were performed by MOPAC 6.0 package,[18a] and *ab initio* calculations by GAMESS (Jan. 1993 version)[19b] at HF or MP2 level using the 3-21G, 6-31G* and 6-31G** basis sets.

Results and Discussion

Acetone-SbF_5.—Vibrational changes induced by complexation of acetone and [$^2H_6$]acetone are shown in Fig. 1. The most indicative change is a shift of the carbonyl stretching frequency to lower values by 115 cm^{-1}. A lowering of the stretching frequency of C–H bonds by 80 cm^{-1} observed in the methyl groups can be assigned to hyperconjugation[19] in conjunction with the change in the C–C stretching frequency which occurs in the opposite direction (from 1230 to 1275 cm^{-1}). The same changes are observable in the deuteriated sample and are fully consistent with the corresponding resonance structures.



Comparing the vibrational changes in the acetone–SbF_5 complex with those occurring upon ionization of 2-chloropropane to the 2-propyl cation (C–H str. is shifted from 2955 to 2730 cm^{-1}),[20] a qualitative analogy becomes evident. In both cases the C–H stretching vibration is shifted to lower and the C–C stretching to higher wavenumbers. Although the shifts are more pronounced in the cation, SbF_5 complexes of ketones evidently can serve as good qualitative models for studying electronic effects on the stability of a positively charged carbon atom.

Structural Effects.—Using Sieberts semiempirical correlation[21] and the experimentally determined carbonyl stretching frequencies (Table 1), the C=O bond lengths and bond orders of ketones **1**–**23** and their SbF_5 complexes could be calculated. In all cases bond lengths increase and bond orders decrease upon complexation. The calculated carbonyl bond length difference between adamantanone **22** and the adamantanone complex (0.043 Å) compares well with the corresponding crystal structure data determined by Laube[9] (0.045 Å).

By taking the number of adjacent C–C bonds (N) as a structural parameter no simple relationship exists between the topological structure of a ketone or its SbF_5 complex and their carbonyl stretching frequencies. However, a correlation with the structure can be found by looking at $\Delta\nu$, the measured difference in the C=O stretching frequencies of the ketone and the ketone complex. The parameter $\Delta\nu$ can serve as a quantitative measure of the electron perturbation in the hydrocarbon skeleton caused by the development of a partially positive charge on the carbonyl carbon atom.

The relationship of $\Delta\nu$ *vs.* N for ketones **1**–**23** is shown in Fig. 2. The $\Delta\nu$ values for ketones **1**–**3**, **8**–**10**, **12** and **15** which are structurally similar to simple, classical carbocations, *i.e.* those

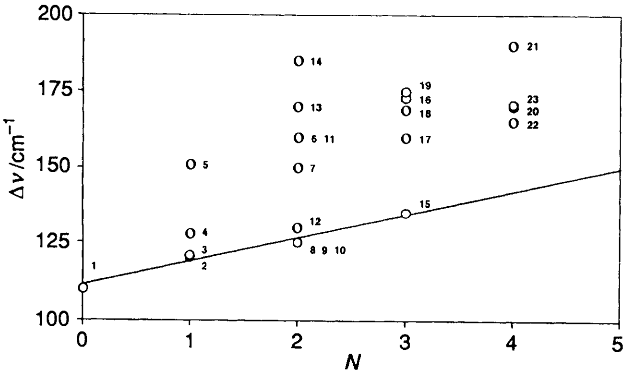


Fig. 2 Relationship of experimental $\Delta\nu$ [$\nu_{C=O}$(ketone) − $\nu_{C=O}$(complex)] *vs. N* for the structures **1–23**: $\Delta\tilde{\nu}$/cm^{-1} = 7.77*N* + 111.3, *r* = 0.965

Table 2 Calculated differences in C=O bond lengths (Δl/Å) and stretching frequencies ($\Delta\nu$/cm^{-1}) of selected ketones from Table 1 and corresponding protonated forms

	AM1		RHF/3-21G	
Ketone	Δl	$\Delta\nu$	Δl	$\Delta\nu$
1	0.0767	326	0.0648	221
2	0.0764	326	0.0652	229
3	0.0768	327	0.0653	230
5	0.0773	325		
6	0.0846		0.0886	
7	0.0701	285	0.0638	253
8	0.0736	298	0.0657	245
9	0.0770	333	0.0693	
10	0.0779	339		
15	0.0728	297	0.0661	252
16	0.0763	331		
18	0.0761	331		
19	0.0727	295		
20	0.0686	281		
21	0.0726	299		
22	0.0740	318		
23	0.0746	324		

solvolysing by k_c and/or k_s mechanisms[22] correlate reasonably well with *N*, the number of adjacent C–C bonds ($\Delta\nu$/cm^{-1} = 7.77 *N* + 111.3; *r* = 0.965, st.dev. = 2.1 cm^{-1}) (Fig. 2). Since *N* correlates with $\Sigma\sigma_I$, in the absence of other effects, one could interpret the increase of $\Delta\nu$ with *N* as being caused by the inductive donation of electrons from C_α–C_β bonds and therefore related only to the topology of the ketone.

Points that noticeably deviate from the line in Fig. 2 (**4–7**, **11**, **13**, **14**, **16–23**) belong to complexes of ketones structurally related to carbocations in which other stabilizing mechanisms in addition to inductive effects are operative. Transannular hydrogen bridging, well established in the cyclooctyl cation[23] is likely to be responsible for the frequency shift in the complex of **11**, while the largest deviation from the straight line is observed with the homoaromatically stabilized complex of **14**.[24] The other structures are related either to classical 'non-classical' cations[25] (**6**, **19**, **21**) or cations where this interaction is smaller or where a variable degree electron donation occurs by a combination of hydrogen and carbon bridging (**11**, **13**, **16**, **18**, **20**, **22** and **23**). Computational results described below seem to support this interpretation.

The two methyl substituted ketones **16** and **23** which differ only in *N*, but show practically the same shift (173 and 171 cm^{-1}, respectively) demonstrate both the sensitivity of measurements, and the non-additivity of hyperconjugative interactions.[6b]

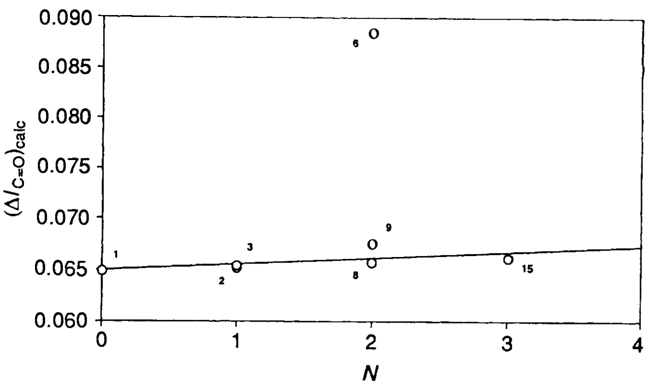
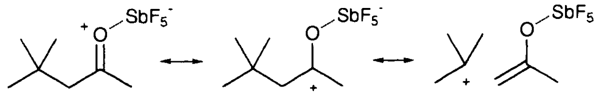


Fig. 3 Relationship of calculated Δl[$l_{C=O}$(ketone) − $l_{C=O}$(complex)] *vs. N* for the structures **1–3**, **6–9** and **15** (RHF/3-21G)

Methyl substituted pentanones **4** and **5** present examples with an identical number of adjacent C_α–C_β bonds (*N*) but a different degree of stabilization by the adjacent methyl groups. Ketone **5** can be regarded as a model for the neopentyl cation.



Cyclobutanone (**7**), which is slightly puckered, undergoes a conformational change upon complexation, allowing an electron delocalization similar to but smaller than in the parent bicyclobutonium ion.

Computational Results.—Semiempirical calculations (AM1 and PM3) were performed for (*i*) ketones **1–23**, (*ii*) protonated ketones, and (*iii*) corresponding BF_3 and SbF_5 complexes (PM3 only). Although in all cases an elongation of the C=O bonds and a shortening of the C–C(O) bonds was observed upon complexation, no quantitative correlation of the calculated and experimental C=O stretching frequency was detected. Preliminary calculations at *ab initio* HF/3-21G and HF/6-31G* levels of simple aldehydes and ketones and their BF_3 and SbF_5 complexes showed that protonated ketones can be taken as computationally feasible models for SbF_5 complexes. Structure and vibrational spectra of ketones **1–3**, **6–9** and **15** and their protonated forms were obtained by full optimization at HF/3-21G level, and of ketones **1–3** and **6–8** at HF/6-31G* level. Calculated differences in C=O bond lengths (Δl) and stretching frequencies ($\Delta\nu$) of ketones **1–9**, **15–16** and corresponding protonated forms are given in Table 2. Although correlation of calculated and experimental C=O frequency shifts at HF/3-21G level is not very good, changes in C=O bond lengths qualitatively follow the experimental results. The calculated changes of bond lengths for ketones **1–3**, and **7**,**8** linearly correlate with the topological parameter *N* (Fig. 3). However, the point for cyclopropylmethyl ketone (**6**) markedly deviates from the line, as was the case with the experimental $\Delta\nu$ *vs. N* correlation. Only qualitative different from the experiment are the values for cyclobutanone (**7**), indicating that for an adequate theoretical description of its SbF_5 complex, the inclusion of electron correlation is neccessary.

Conclusions

In summing up, the following conclusions can be drawn from the results described in this paper. Electronic effects influencing the stability of carbocations can also be detected though to a lesser degree in complexes of ketones with antimony pentafluoride. The shift in the carbonyl stretching frequency of the complex relative to the parent ketone gives a qualitative measure of this interaction. Simple ketones related to carbocations which are formed by k_c and/or k_s processes show shifts which are linearly correlated with the number of adjacent C–C bonds and can be ascribed to inductive stabilization. Ketones related to carbocations where additional stabilization occurs by hyperconjugation, homoaromaticity, carbon or hydrogen bridging deviate from the linear relationship by a degree qualitatively related to this stabilization. Crystallographic data of isolated ketone complexes, solvolytic and stereochemical results, as well as computational data on model systems, support this contention.

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