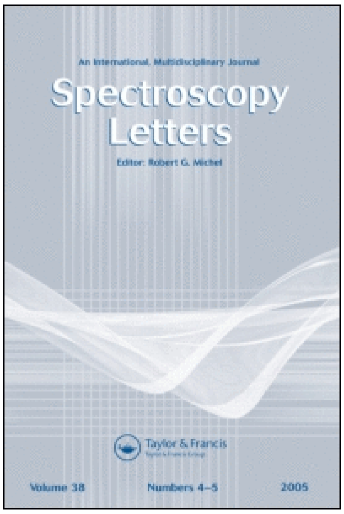

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Infrared Spectra of Negative Ions of Amides

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INFRARED SPECTRA OF NEGATIVE IONS OF AMIDES

KEY WORDS: Infrared spectra; Amides; N-anions; Band assignment.

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ABSTRACT

The anionic derivatives of a series aliphatic, arylaliphatic and aromatic compounds containing amide group were investigated by means of infrared spectroscopy. The stretching vibration frequencies of the amide C=O, the ketone C=O and the N-C(Ph) in the N-anions of the studied compounds were assigned: the amide C=O shifts 76-180 cm^{-1} downward depending on the substituents; the band intensity increases 2.5-3 times. It was found an excellent correlation between the carbonyl stretching vibration frequencies of the studied N-anions with the Hammett σ^- constants of the substituents.

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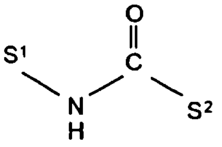
INTRODUCTION

There exist in literature spectral and theoretical studies on the anionic derivatives of cyclic compounds like phthalimide[1,2], succinimide[2], saccharin[3-5], maleimide[6]. About 150 cm^{-1} downward frequency shift of the asymmetrical amide carbonyl band is established for the potassium (sodium) phthalimide[1,2]. Noncyclic aromatic and arylaliphatic amides are investigated in order to determine some substituent constants of the metallated amide groups[7,8] and it is pointed out that the electronic effect of these groups depends on the way they connect with the substituted aromatic ring (N-aryl or aryl-CO): the frequency of the amide carbonyl group of the trans-α-phenyl-β-4-acetylaminophenylacrilonitrile shifts about 200 cm^{-1} downward, however ν(CO)[9] is not assigned.

The aim of the present study is a systematic investigation of the anionic derivatives of a series compounds containing amide group by means of infrared (IR) spectra:



S^1 = H, cyclohepthyl, $C_6H_5CH_2$, C_6H_5, 4–$CH_3COC_6H_4$, 3–$CH_3COC_6H_4$, 3,4-$(OCH_3)_2C_6H_3(CH_2)_2$, 4–$NO_2C_6H_4$, 4–$^{15}NO_2C_6H_4$, 2,6–$(CH_3)_2C_6H_3$, 2,6–$(CH_3,C_2H_5)C_6H_3$, 4–CNC_6H_4.

S^2 = CH_3, $ClCH_2$, Cl_3C, $C_6H_5CH_2$, 3,4-$(OCH_3)_2C_6H_3CH_2$, 4-$NO_2C_6H_4CH_2$, C_6H_5, 3,4-$(OCH_3)_2C_6H_3$.

EXPERIMENT

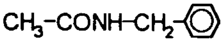
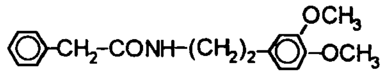
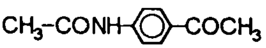
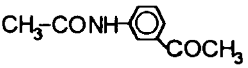
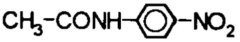
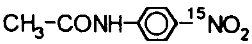
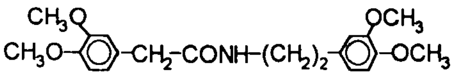
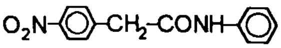
The compounds containing amide group were synthesized according to the literature[10]. The N-anions were obtained by reacting the studied compounds (20mg/ml) in dry dimethylsulfoxide (DMSO) or in DMSO-d_6 in some cases with dry sodium methoxide ($NaOCH_3$) or dimsyl sodium under pure argon[8,11] The IR spectra were registered on a Perkin-Elmer 1750 spectromether in CaF_2 cell at 2 cm^{-1} resolution. The band frequencies ν(CO) of the parent amides and the frequencies ν(CO) of the amide ions as well as the frequencies of the stretching vibration of the N-C(Ph) bond and the keton group frequencies of the respective N-anions are presented in the Table. The relative intensity of the bands is determined as well.

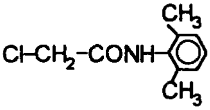
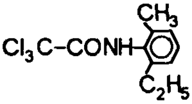
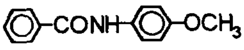
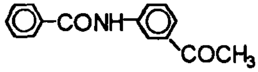
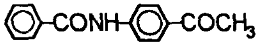
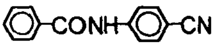
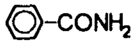
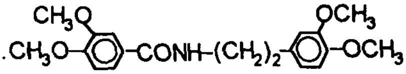
RESULTS AND DISCUSSION

The IR spectra of the compounds containing amide group show that the band of the carbonyl stretching vibration of the parent amides ν(CO) appears in a 1647 cm^{-1} ÷1712 cm^{-1} frequency region, depending on the substituents. When another carbonyl group is present, a ketone one (6 and 18 in the Table), more bands are observed at the given region. The band at 1696 cm^{-1} (6 in the Table) is assigned as a band of the ν(CO) stretching vibration of the amide group, while the band at 1674 cm^{-1} for the ketone group. The IR spectrum of the compound 18 possesses three bands in this region: at 1704cm^{-1}, 1683 cm^{-1} and 1669 cm^{-1}. The first one is assigned to the amide carbonyl, the 1683 cm^{-1} band - to the ketone group, the lowest frequency band is probably a result of any conformer. In the case of amides 7 and 19 where a ketone group exists as well, only one band at 1682 cm^{-1} is observed for ν(CO): the shape of the band is asymmetrical obviously due to the overlapping of the carbonyl groups of compound 7; both carbonyl group bands in the spectrum of compound 19 coincide completely and only one band at 1674 cm^{-1} is observed.

The metallation of the parent compounds leads to a decrease of the ν(CO) band intensity or to the complete disappearance of the band and new very strong ν(CO) bands appear simultaneously in the low frequency region.

TABLE

Compound	Neutr. comp.	Amide ion in DMSO	
	ν_{CO} [cm^{-1}]	ν_{CO} [cm^{-1}]	$\nu_{N-C(Ph)}$ [cm^{-1}]
1. $CH_3{-}CONH_2$	1677	1553 [2]1556vs	
2. 	1662	[2]1559vs	
3. 	1669	1553	
4. 	1666	1556	
5. 	1687	1533vs [2]1532vs	1383s [2]1382s
6. 	1696 1674	1518vs [3]1652s	1372s
7. 	1682	1531s [3]1671m	1378m
8. 	1700	1532s	1376s
9. 	1700	1532s	1374s
10. 	1698	1532m	1369m
11. 	1687	1530m	1352m

12. 	1690	1569s	1367s
13. 	1707	1624s ^{2}1624s	
14. 	1711	1635s	1324m
15. 	1712	1624s ^{1,2}1623vs	1330m ^{1,2}1330s
16. 	1667	1526vs ^{2}1527vs	1365vs ^{2}1365vs
17. 	1662	1530s	1362s
18. 	1704 1683 1669	1524s ^{3}1671m	1367s
19. 	1674	1514vs 1651s	1364vs ^{2}1362s
20. 	1667	1517vs	1365vs
21. 	1679	^{1,2}1534m ^{1,2}1529s	
22. 	1676	1533m	
23. 	1647	1543m	

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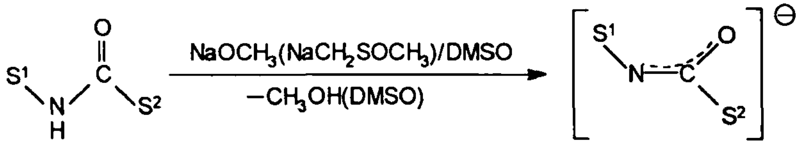
[1] The spectra are registered in DMSO-d_6. [2] With dimsyl-sodium. [3] ν(CO) of the ketone group.

The conversion of the parent amides, containing aliphatic or arylaliphatic substituents (1-4 in the Table) into N-anions with sodium methoxide results



into an intensity decrease of ν(CO) band of the parent compound and to the appearance of a new broad strong band at 1553 cm^{-1} ÷1556 cm^{-1}.

The studied amides' metallation with the stronger base dimsyl-sodium leads to the total disappearance of the ν(CO) band of the parent compounds 1 and 2, which marks out that the reaction practically proceeds entirely. The new broad and very strong band turns out at the same frequency like the bands of the products treated with sodium methoxide. This result confirms the reproduction of the same species irrespectfully to the metallating agent used in both cases. When treating the corresponding amides with dimsyl-sodium a considerable decrease of the band intensity to entire disappearance of the bands ν(NH) and δ(NH) is observed also. In the IR spectra of the products obtained by metallation with $NaOCH_3$, a band at ~3400 cm^{-1} is observed, owing to the O-H stretching vibration of the separated methanol. The data obtained prove the conclusion that the metallation of these amides produces N-anions, whose IR spectra show a band of the amide carbonyl group at 1553 cm^{-1} ÷1559 cm^{-1}.

The reaction of the parent compounds with $NaOCH_3$ where S^1 next to the nitrogen atom of the amide group is phenyl or aryl group (5-15), is practically followed by a complete conversion into N-anions; IR spectral bands for the parent amide are not seen. In 1518 cm^{-1}÷1635 cm^{-1} and in 1330 cm^{-1} ÷1383 cm^{-1} regions appear new bands - from medium to strong.

When S^2 next to the carbon atom of carbonyl group is phenyl or aryl group (21÷23) in the IR spectra of their amide ions new bands are detected in the 1534 cm^{-1} ÷1543 cm^{-1} frequency region.

The IR spectra of the anionic products of compounds 16÷20, where the substituents S^1 and S^2 are aryl and phenyl group respectively, show bands in the same frequency regions like those of the compounds 5÷15.

The metallation of the amides containing ketone group leads to a decrease of the amide carbonyl frequency and sequently to the ketone one. The decrease of the frequency of the ketone group at 3-position (7 and 18 in the Table) being 11-12 cm^{-1} appears at 1671 cm^{-1}, while the frequency decrease of ν(CO) at 4-position is 23 cm^{-1} (6 and 19); the band appears at 1651 cm^{-1} in the IR spectra of the respective amide ions. The registered ν(CO) frequencies of the ketone group in the IR spectra of the N-anions of studied amides are in excellent agreement with the literature data[12].

The bands of the reduction products of the studied compounds in 1518 cm^{-1} ÷1635 cm^{-1} interval are assigned to the carbonyl group of the amide ion whereas the bands in the 1330 cm^{-1} ÷1383 cm^{-1} region - to the stretching N-C(Ph) vibration. The assignment is made on the basis of similarity between the studied compounds. It is seen from the data in the Table that the ν(CO) band frequency of the amide ions is not influenced substantially when the aliphatic substituents of compounds 1÷4 are substituted with arylaliphatic ones. The introduction of phenyl or aryl group bonded with the nitrogen atom of the amide group and phenyl group connected with the carbon atom of the carbonyl amide group leads to a decrease of the established frequency interval with 30 cm^{-1} and to a rise of new bands in the 1330÷1383 cm^{-1} region; the bands intensity in almost all the cases is proportional of the amide carbonyl group in the respective amide ions: the bands are assigned to the stretching vibration of the N-C(Ph) bond. It is seen in the Table that the IR spectra of the N-anions of the studied compounds containing phenyl or aryl group next only to the amide carbonyl group (21÷23), bands in the frequency region 1330÷1383 cm^{-1} are not observed.

The presence of the $ClCH_2$- or Cl_3C- group (12÷15), next to the amide carbonyl increases the ν(CO) frequency of the amide ion to 1635 cm^{-1} as a result of the strong negative inductive effect of these groups. It is important to note that ν(CO) of the N-anions of the compounds 13 and 15 are equal (1624 cm^{-1}) although the substituent next to the nitrogen atom is a benzyl group in 13 and phenyl group in 15: thus no influence on the ν(CO) is observed.

The conversion of the amides containing aromatic rings in the respective N-anions gives rise to frequency changes of the ν_8 and ν_{19} (according to the Wilsons' notation[13]) bands of the aromatic rings. When the aromatic ring is connected with the nitrogen atom of the amide group, the metallation of the corresponding amide provokes certain changes of the ν_{19} vibrations: the intensity of the bands considerably increases and the frequency decreases with 10÷20 cm^{-1}. Relatively stable are the ν_8 vibrations, excluding p-NO_2 substituted compounds (8 and 9), where the ν_8 frequency decreases to 1565 cm^{-1}.A substantial increase of the intensity and decrease of the ν_8 and ν_{19} frequencies are observed in the amide ions of the compounds containing benzene rings as S_1 and S_2. The basic reason for intensity increase of the stretching vibrations of the phenyl rings is the higher mobility of the negative charge over the conjugated system.

The measurement of the integrated intensity of the ν(CO) band of N-anions is rather complicated in view of the appearance of the considered bands in the frequency region of ν_8 and ν_{19} vibrations of the benzene rings; the bands could not be diststinguished because of a partial overlapping. The intensity of the bands is defined relatively to the intensity of the other bands in the IR spectrum of the corresponding anionic derivatives. When the band position allows measuring its integrated intensity (e.g. 2 and 5 in the Table) a 2.5-3 fold increase of the carbonyl group band intensity is observed in the N-anions compared to the respective parent compounds.

The substituents (H, OCH_3, $COCH_3$, CN) at 3- or 4- position in the benzene ring next to the nitrogen atom of the amide group in the N-anions of aromatic amides (16÷20) effect on the carbonyl group band frequency according to the values of their σ^- constants. The relationship ν_{CO}/σ^- of the amides anions results in a correlation equation with excellent correlation coefficient $r = 0.992$ ($\rho = -9.352$, $n = 5$).

CONCLUSION

The interaction between the studied amides and sodium methoxide or dimsyl sodium in DMSO under pure argon forms the respective N-anions. The frequency of the amide carbonyl group in the IR spectra of the obtained N-anions decreases to 180 cm^{-1} depending on the substituents S^1 and S^2. The frequency region of the ν(CO) band in the studied N-anions is 121 cm^{-1}, therefore the electronic and steric factors on the ν(CO) are almost twofold stronger in the N-anions than in the parent compounds.

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