COMMUNICATIONS

DE LA FACULTÉ DES SCIENCES
DE L'UNIVERSITÉ D'ANKARA

Série B: Chimie

TOME : 27 ANNÉE : 1981

A LA MEMOIRE D'ATATÜRK AU CENTENAIRE DE SA NAISSANCE

Thermodynamic data for the effect of substituents on the strength of Hetero-Intermolecular Hydrogen Bonds. Part II.

by

A. A. TAHA, W. S. HIGAZY and A. M. EMARA

23

Faculté des Sciences de l'Université d'Ankara
Ankara, Turquie

Communications de la Faculté des Sciences de l'Université d'Ankara

---

La Revue "Communications de la Faculté des Sciences de l'Université d'Ankara" est un organe de publication englobant toutes les disciplines scientifique représentées à la Faculté.

La Revue, jusqu'à 1975 à l'exception des tomes I, II, III, etait composé de trois séries

Série A : Mathématiques, Physique et Astronomie.
Série B : Chimie.
Série C : Sciences naturelles.

A partir de 1975 la Revue comprend sept séries:

Série A_1: Mathématiques
Série A_2: Physique
Série A_3: Astronomie
Série B : Chimie
Série C_1: Géologie
Série C_2: Botanique
Série C_3: Zoologie

En principe, la Revue est réservée aux mémoires originaux des membres de la Faculté. Elle accepte cependant, dans la mesure de la place disponible, les communications des auteurs étrangers. Les langues allemande, anglaise et française sont admises indifféremment. Les articles devront être accompagnés d'un bref sommaire en langue turque.

Adresse: Fen Fakültesi Tebliğler Dergisi, Fen Fakültesi, Ankara, Turquie.

DEDICATION TO ATATÜRK'S CENTENNIAL

Holding the torch that was lift by Atatürk in the hope of advancing our Country to a modern level of civilization, we celebrate the one hundredth anniversary of his birth. We know that we can only achieve this level in the fields of science and technology that are the wealth of humanity by being productive and creative. As we thus proceed, we are conscious that, in the words of Atatürk, "the truest guide" is knowledge and science.

As members of the Faculty of Science at the University of Ankara we are making every effort to carry out scientific research, as well as to educate and train technicians, scientists, and graduates at every level. As long as we keep in our minds what Atatürk created for his Country, we can never be satisfied with what we have been able to achieve. Yet, the longing for truth, beauty, and a sense of responsibility toward our fellow human beings that he kindled within us gives us strength to strive for even more basic and meaningful service in the future.

From this year forward, we wish and aspire toward surpassing our past efforts, and with each coming year, to serve in greater measure the field of universal science and our own nation.

Thermodynamic Data for the effect of substituents on the strength of Hetero-Intermolecular Hydrogen Bonds. Part II.

A. A. TAHA, W.S. HIGAZY and A. M. EMARA

Department of Chemistry, University College for Girls, Ain Shams University, Cairo, Egypt

(Received July 30, 1981; accepted October 16, 1981)

SUMMARY

Hetero-association constants and enthalpy changes are estimated for the hetero-association reactions between trifluoroacetic acid and each of p-nitro and p-meythylbenzophenones, at the temperature range 35–55 . The results show that the presence of the p-nitro group in the benzophenone molecule weakens the hydrogen bonds formed between trifluoroacetic acid and benzophenone, whereas the p-methyl group strengthens such bonds.

INTRODUCTION

In Part I of this series[1] we have reported on the effect of the p-chloro and the p-bromo groups on the strength of the heterohydrogen bonds formed between trifluoroacetic acid (TFA) and benzophenone, by computing and comparing values of enthalpy changes ($\triangle$ H) for the hetero-association reactions between TFA and each of the unsubstituted and substituted benzophenones. Since that study proved to be in accordance with the expected operating powers of the substituent groups[2], we extended the investigation in the present work to the study of the effect of some new substituents on the strength of the hydrogen bonds formed between TFA and benzophenone. The substituents are the p-nitro and the p-methyl, and were chosen on the basis of differences in the operating powers expected to affect the basicity of the carbonyl group to hydrogen bond with TFA.

EXPERIMENTAL AND METHODS OF CALCULATION

The same experimental procedure employed in Part I was followed in the present work[1,8–7]. It is based on the measured vapour pressure and on the resulting vapour phase equilibria[8] of added increments of a volatile solute (TFA in our case) over a solution of this solute, either alone, or with a nonvolatile solute (the phenone in our case), in a nonvolatile, nonpolar solvent. Diphenylmethane was used as the solvent in the present study. The present investigation was carried out at 3 concentrations of each phenone, 0.05, 0.1 and 0.2 molar, and over the temperature range 35–55 : for each concentration.

Also, the same methods of calculations adopted in Part I[1] were followed in the present work, where the experimental data were fitted by a computer program designed for linear and nonlinear least squares. The data were best fitted by assuming the formation of a 1:1 and 2:1 hetero-hydrogen bonded TFA: phenone complexes, for which formation constants K_{11} and K_{21} were computed respectively, at each temperature. Enthalpies of formation (△ H) of the heterocomplexes were calculated from the temperature dependence of the computed formation constants.

RESULTS AND DISCUSSION

Table 1 summarizes the least squares values for the heteroassociation constants K_{11} and K_{21} for each system, at each of the 3 temperatures. It also includes the least square values for $\triangle H_1$ and $\triangle H_2$, the enthalpies of formation of the 1:1 and 2:1 hetero-complexes, respectively, in each system. Table 2 includes previously reported values[1] of enthalpy changes for the TFA: benzophenone, TFA: p-chlorobenzophenone and TFA: p-bromobenzophenone systems, which will be needed for compa-

Table 1

TFA with	Temp. (°C)	K_{11} (molar^{-1})	K_{21} (molar^{-2})	$\triangle H_1$ k. cal/ mol of	$\triangle H_2$ of complex
p-Nitrobenzophenone	35	5.46±0.61	114.3±10.32	-4.95 ±0.46	-9.63 ±0.72
	45	4.11±0.42	79.7±7.51		
	55	3.34±0.40	45.2±5.11		
p-Methylbenzophenone	35	57.5±2.62	533.8±39.93	-15.33 ±0. 5	-16.31 ±0.37
	45	22.8±1.08	237.5± 9.77		
	55	11.9±0.49	107.8± 3.33		

Table 2*

TFA with	$\triangle H_1$ K cal/mol	$\triangle H_2$ of complex
Benzophenone	-13.46 ± 0.24	-14.94 ± 0.26
p-Bromonenzophenone	-8.46 ± 0.14	-12.25 ± 0.19
p-Chlorobenzophenone	-7.70 ± 0.15	-11.43 ± 0.18

* previously reported in Part I(1)

rison purposes with comparable values obtained in the present work. The experimental monomer vapour pressures measured for successive formal concentrations of TFA for the different systems, are included in Tables 3 and 4.

If we first compare the $\triangle$ H values for the two systems under investigation with those for TFA: benzophenone system, it can be seen that the values for the TFA: p-nitrobenzophenone system are less, whereas those for the TFA: p-methylbenzophenone system are more, than the values for the TFA: benzophenone system. Hence, it can be concluded that the presence of the p-nitro group in the benzophenone molecule weakens the hetero-hydrogen bonds formed between the latter and TFA molecules, whereas the presence of the p-methyl group strengthens such bonds. The extent of weakening or strengthening can be estimated from the difference in the values of $\triangle$ H.

Another conclusion can be drawn from comparing the values of $\triangle$ H for the TFA: p-nitrobenzophenone system (Table 1), with those obtained previously for TFA: p-chlorobenzophenone and TFA: p-bromobenzophenone system (Table 2), since the p-nitro group was found to weaken the hetero-hydrogen bonds, similar to the p-chloro and the p-bromo groups. Such comparison shows that the p-nitro group exhibits a stronger weakening effect on the hetero-hydrogen bonds, i.e. a stronger hindering effect on the formation of such bonds. This is judged from the smaller values of $\triangle$ H for the p-nitro group as with those in case of presence of the p-chloro or the p-bromo groups.

The conclusions reached can be explained on the basis of the effect of the operating powers of the substituent groups. In case of the nitro group, its – I and –R effects, which were discussed before in detail,[9] will both contribute to the decrease of the potency of the lone pairs of electrons on the carbonyl-oxygen to hydrogen bond. Such an effect will

Table 3

System TFA/p-Nitrobenzophenone

$f^{TFA} \times 10^2$ (molar)	P_M^{TFA} (torr)									
	35			45			55			Temp. °C
	0.05	0.10	0.20	0.05	0.10	0.20	0.05	0.10	0.20	[Phenone] M
1.347	0.89	0.75	0.58	1.41	1.18	0.92	2.03	1.86	1.31	
2.693	1.67	1.54	1.03	2.74	2.43	1.79	4.06	3.66	2.74	
4.040	2.74	2.20	1.58	3.95	3.74	2.61	5.93	5.47	4.14	
5.386	3.13	3.01	2.35	5.09	4.84	3.61	7.83	7.25	5.61	
6.733	3.90	3.72	2.64	6.26	6.01	4.43	9.78	8.86	7.01	
8.080	4.67	4.42	3.14	7.38	7.08	5.37	11.51	10.81	8.28	
9.426	5.37	5.09	3.68	8.58	8.25	6.19	13.28	12.47	9.41	
10.770	6.05	5.75	4.18	9.61	9.32	7.14	14.89	14.15	10.78	
12.120	6.75	6.42	4.69	10.73	10.40	7.85	16.60	15.89	12.12	
13.460	7.55	7.07	5.18	11.79	11.44	8.71	18.25	17.44	13.34	
14.810	8.02	7.71	5.66	12.84	12.47	9.84	19.83	18.98	14.63	
16.150	8.79	8.31	6.24	13.82	13.48	10.34	21.43	20.51	15.83	
17.500	9.30	8.91	6.69	14.88	14.21	11.03	22.95	22.00	17.04	
18.850	9.91	9.46	7.16	15.97	15.30	11.72	24.47	23.38	18.13	
20.211	10.34	9.98	7.63	16.75	16.21	12.49	25.94	24.84	19.43	

Table 4

System TFA/p-Methylbenzophenone

TFA $f \times 10^{2}$ (molar)	p_MTFA (torr)									
	35			45			55			Temp. °C.
	0.05	0.10	0.20	0.05	0.10	0.20	0.05	0.10	0.20	[Phenone] M
1.347	0.91	0.23	0.43	0.98	0.58	0.44	1.56	1.15	1.289	
2.693	1.64	0.82	0.76	2.25	1.33	0.92	3.18	2.30	2.42	
4.040	2.24	1.25	0.89	3.42	2.22	1.41	4.83	3.40	3.10	
5.386	2.98	1.83	1.20	4.55	2.94	1.91	6.83	4.81	4.05	
6.733	3.63	2.32	1.30	5.80	3.96	2.34	8.33	5.97	4.84	
8.080	4.23	3.00	1.55	6.66	4.78	2.69	10.20	7.58	5.79	
9.426	4.91	3.53	1.69	8.13	5.75	3.23	11.84	8.92	6.70	
10.770	5.49	4.25	1.90	9.32	6.70	3.75	13.63	10.34	7.47	
12.120	6.22	4.85	2.19	10.46	7.72	4.19	15.42	11.79	8.35	
13.460	6.76	5.51	2.52	11.62	8.70	4.67	17.01	13.27	9.24	
14.810	7.44	6.13	2.78	12.72	9.65	5.11	18.68	14.73	10.02	
16.150	7.85	6.75	3.05	13.75	10.65	5.62	20.31	16.24	10.87	
17.500	8.63	7.35	3.33	14.79	11.68	6.11	22.03	17.79	11.76	
18.850	9.18	7.95	3.60	15.80	12.66	6.65	23.52	19.26	12.61	
20.211	9.89	8.54	3.91	16.84	13.62	7.19	24.04	20.69	13.54	

be more powerful than the operating effects in case of either the chloro or the bromo groups[2,9]. On the other hand, the methyl group exhibits a + I effect, not opposed by any other effect in case of the p-methylbenzophenone, thus increasing the electron density on the carbonyl-oxygen, which explains the increased power of hydrogen bonding with TFA molecules than for the unsubstituted benzophenone.

REFERENCES

1- **Taha, A.A., Higazy, W.S. and Emara, A.M.,** Egypyt. J. Chem., accepted.

2- **Taha, A.A., Kamel, Kh. M. and Emara, A.M., J.** Ind. Chem. Soc., 1979, 56, 839.

3- **Taha, A.A., Grigsby, H.D., Johnson, J.R., Christioan, S.D. and Affsprung, H.E., J..** Chem. Educ., 1966, 43, 432.

4- **Higazy, W.S. and Taha, A.A., J.** Phys. Chem., 1970, 74, 1982.

5- **Taha, A.A. and Christian, S.D., J.** Phys. Chem., 1969, 73, 3430.

6- **Taha, A.A. and Christian, S.D., J.** Phys. Chem., 1970, 74, 3950.

7- **Taha, A.A., Higazy, W.S. and Christian, S.D., J.** Ind. Chem. Soc., 1976, 53, 793.

8- **Ling, C., Christian, S.D., Affsprung, H.E. and Gray, R.W.,** J. Chem. Soc., 1966, 293.

9- **Taha, A.A. and Abdel-Al, H.E.,** J. Ind. Chem. Soc., 1981, 58, 149.

Prix de l'abonnement annuel

Turquie: 15 TL; Etranger: 30 TL.
Prix de ce numèro: 5 TL (pour la vente en Turquie).
Prière de s'adresser pour l'abonnement à: Fen Fakültesi
Dekanlığı Ankara, Turquie.

Ankara Üniversitesi Basımevi. Ankara - 1982