viewed as one more example of VLPP results agreeing with known high-pressure Arrhenius parameters *via* an estimated A factor and RRKM theory.)

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Thermodynamics of Molecular Association by Gas–Liquid Chromatography. IV. Haloalkane Acceptors with Di-*n*-octylmethylamine and Tri-*n*-hexylamine

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Abstract: Equilibrium constants, enthalpies, and entropies of complex formation between ten haloalkane acceptors and the electron donors di-*n*-octylmethylamine and tri-*n*-hexylamine have been determined by gas–liquid chromatography in the temperature range 30 to 60°. The results are discussed in terms of the possible contributing forces of stabilization for complex formation and are compared with those previously obtained with the electron donors di-*n*-octyl ether and di-*n*-octyl thioether.

This paper represents a further contribution to the quantitative study of molecular association in binary nonelectrolyte solutions by means of gas–liquid chromatography (glc). Previously we reported a glc study of the complexes formed between a variety of haloalkane acceptors and the donors di-*n*-octyl ether and di-*n*-octyl thioether.[1] While the initial purpose of this work was to carry out a systematic study of the hydrogen-bonding propensities of the haloalkane systems, the trends observed in the measured equilibrium constants indicated that there was an additional interaction present in many of the systems. This trend was most marked in those systems involving the thioether with bromo-substituted methanes. On the basis of indirect evidence for the existence of stable complexes between halomethanes and n-donors, it was postulated that this additional contribution to the equilibrium constants might be due to a charge-transfer interaction ($n \rightarrow \sigma^*$ type) involving Cl and Br as acceptors with the O and S donors.

It has been well established that tertiary amines form relatively strong H-bonded complexes with haloforms, N being a stronger electron donor than O or S. Direct spectroscopic evidence also exists for the presence of charge-transfer complexes of the $n \rightarrow \sigma^*$ type in solutions of tertiary amines with halomethanes.[2] In fact, it has been postulated that the reaction of chloroform with amines occurs through this mechanism.[3] Thus, a glc study of solutions of haloalkanes in tertiary amines might be expected to yield further evidence of the ability of these types of systems to undergo molecular association *via* two different mechanisms. Accordingly, in the present study we have extended our investigation to those systems involving di-*n*-octylmethylamine and tri-*n*-hexylamine as the electron donors together with the same series of haloalkanes previously used as electron acceptors.[1] The choice of two tertiary amines of differing hydrocarbon chain structure was made with a view to evaluating the effect of electron donor accessibility on the thermodynamic association parameters.

As in the previous study, the method of evaluating the thermodynamic association constants is that devised recently by Martire and Riedl.[4] The validity of this approach and the assumptions made in deriving the expressions used have very recently been critically evaluated in this laboratory.[5] A comparison has been made for some of the systems studied here, between the results obtained using the Martire–Riedl approach[4] and those obtained by using the more general method of Cadogan and Purnell.[6] The conclusion reached from this comparative study was that the former method yields results identical with those obtained from utilization of the Purnell method provided certain explicit conditions are met.[5] These conditions are, in general, fulfilled for the systems involved in the present and previous[1] studies. Thus the Martire–Riedl approach remains our method of choice for these systems since it has the advantage of much greater speed at comparable precision.

The method of extracting the thermodynamic association parameters from glc measurement of specific retention volumes has already been described in detail in previous papers.[1,4]

Experimental Section

Liquid Phases. The electron donors di-*n*-octylmethylamine (DOMA) and tri-*n*-hexylamine (THA) were obtained from Eastman Chemical Co. Both amines required further purification; this was done by fractional distillation at reduced pressure on a Nester-Faust spinning band column. The major fraction collected of the di-*n*-octylmethylamine had a bp of 114° at 0.8 mm while that

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of the tri-*n*-hexylamine had a bp of 125° at 1.0 mm. These fractions were analyzed by high-temperature glc using an SE 30 column under isothermal conditions at 200°, and both proved to have a purity in excess of 99%. The amines were then stored in dark containers in a refrigerator in order to minimize their tendency to decompose. The densities of the donors at the experimental temperatures are required for the determination of the association constant, *K*. These were determined by pycnometry and the data are listed in Table I.

Table I. Densities (g/ml) of the Pure Electron Donors[a]

	30.0°	40.0°	50.0°	60.0°
Di-*n*-octylmethylamine	0.791	0.785	0.778	0.771
Tri-*n*-hexylamine	0.792	0.786	0.779	0.772

[a] All temperatures in °C here and in following tables.

Solutes. The electron acceptors and alkane solutes selected for this study are identical with those considered in our previous study,[1] with the exception of CBr_4 which was not studied here.

Preparation of Columns. The solid support material used was Johns-Manville Chromosorb W, 60–80 mesh, acid washed, and DMCS treated. Two different coatings were made with each liquid phase, one containing about 8% by weight liquid phase and the other about 15%. The exact liquid weight percentages were determined by an ashing procedure previously described.[4] The coated supports were packed into 0.25-in. o.d. copper tubing. Column lengths of about 5 ft were used for the moderate retention time solutes, and lengths of about 2.5 ft were used for the long retention time solutes.

Apparatus and Procedure. The glc apparatus used in this work is described elsewhere.[4,7] In the present study the detector block temperature was held at about 250° and the injection port at about 220°. The column bath temperature was controlled and measured to within ±0.05°. The general procedure used for obtaining meaningful and accurate specific retention volumes (V_g^0) is also described in a previous paper.[7] Use of the two different liquid loadings enabled us to screen our systems for possible interfacial effects. A representative group of our solutes was studied on both the 8 and 15% loaded columns. No evidence was found for solute adsorption at either the gas–liquid or liquid–solid interfaces. Accordingly, the V_g^0 measurements for the majority of the systems were carried out on one loading (the 8% column).

Results

Specific retention volumes (V_g^0) were determined for each solute with each of the liquid phases at 30.0, 40.0, 50.0, and 60.0° from the average value of at least three separately measured retention times. At the higher temperatures small corrections had to be made for liquid phase loss from the columns. The experimental V_g^0 data (typical standard deviation of about 0.4%) are set out in Tables II and III. The V_g^0 values for the reference solvent, *n*-octadecane, were presented in Table II of ref 1. The values of $(\bar{V}_g^0)_R/(\bar{V}_g^0)_D$, where R refers to the reference solvent and D to the electron donor solvent, were determined by averaging the results for the five alkane solutes studied. These are listed in Table IV. The standard deviations for these average values range from ±0.002 to ±0.008, with a typical value being ±0.005. The pure electron donor concentrations and estimated (through eq 4 of ref 1) activity coefficients are given in Table V. From the data in Tables II through V, the equilibrium constants *K* were computed using eq 2 and 3 of ref 1 and are listed in Tables VI and VII. Through the usual formula for propagation of errors, the standard deviation in *K* is estimated to range from ±0.008 for a *K* of 0.667 to ±0.003 for a *K* of zero. Finally, from the least-squares best-linear fit of ln *K* against reciprocal temperature, the enthalpy and entropy of complex formation were determined for each system. The ΔH and ΔS values, along with the corresponding standard deviations, are listed in Table VIII. Note the relatively larger standard deviations in ΔH and ΔS for the systems with the lower *K* values (carbon tetrachloride and 1,1,1-trichloroethane).

Table II. Specific Retention Volumes with Di-*n*-octylmethylamine

	30°	40°	50°	60°
n-Hexane	406.1	275.8	191.9	136.5
3-Methylpentane	331.2	228.4	161.2	116.1
2,3-Dimethylbutane	270.4	189.1	135.2	98.7
2,4-Dimethylpentane	570.9	379.9	260.5	182.8
3-Methylhexane	943.0	614.6	411.2	281.9
Dichloromethane	154.0	107.6	77.9	57.1
Bromochloromethane	408.4	275.1	190.7	135.5
Dibromomethane	1084	698.5	464.0	318.9
Chloroform	680.3	428.3	279.5	186.7
Dichlorobromomethane	1882	1124	698.0	454.8
Dibromochloromethane	5222	2959	1759	1125
Bromoform	14085	7725	4350	2635
Carbon tetrachloride	713.5	477.0	327.2	233.9
Bromotrichloromethane	2588	1568	984.3	656.5
1,1,1-Trichloroethane	533.9	357.5	250.1	179.1

Table III. Specific Retention Volumes with Tri-*n*-hexylamine

	30°	40°	50°	60°
n-Hexane	417.0	282.5	196.0	139.1
3-Methylpentane	339.5	233.3	164.2	118.0
2,3-Dimethylbutane	277.3	193.0	137.3	99.7
2,4-Dimethylpentane	582.4	389.5	267.2	187.5
3-Methylhexane	970.1	630.4	420.8	287.8
Dichloromethane	125.2	89.6	66.1	49.7
Bromochloromethane	328.2	225.3	159.3	115.6
Dibromomethane	838.6	555.0	376.9	263.7
Chloroform	466.8	305.5	205.9	143.0
Dichlorobromomethane	1243	783.6	503.9	339.0
Dibromochloromethane	3264	1965	1225	788.0
Bromoform	8500	4864	2900	1791
Carbon tetrachloride	667.4	448.0	308.0	219.5
Bromotrichloromethane	1987	1250	810.3	546.8
1,1,1-Trichloroethane	499.1	340.9	238.1	171.6

Table IV. Average Values of $(\bar{V}_g^0)_R/(\bar{V}_g^0)_D$[a]

	30°	40°	50°	60°
n-Octadecane/di-*n*-octylmethylamine	1.004	1.012	1.018	1.024
n-Octadecane/tri-*n*-hexylamine	0.979	0.988	0.997	1.005

[a] The ratio of the specific retention volume of an alkane in the reference (R) solvent to that in the electron donor (D) solvent.

Table V. Concentrations (C_D) and Estimated Activity Coefficients (γ_D) of Pure Electron Donors

	30°	40°	50°	60°
Di-*n*-octylmethylamine				
C_D (mol l.$^{-1}$)	3.096	3.072	3.045	3.018
γ_D	1.000	0.993	0.986	0.981
Tri-*n*-hexylamine				
C_D (mol l.$^{-1}$)	2.939	2.916	2.890	2.865
γ_D	1.081	1.072	1.062	1.054

(7) Y. B. Tewari, D. E. Martire, and J. P. Sheridan, *J. Phys. Chem.*, 74, 2345 (1970).

Table VIII. Enthalpies (kcal/mol) and Entropies (eu) of Complex Formation

	Di-*n*-octylmethylamine		Tri-*n*-hexylamine	
	$-\Delta H$	$-\Delta S$	$-\Delta H$	$-\Delta S$
Dichloromethane	2.41 ± 0.06	11.10 ± 0.20	1.81 ± 0.10	10.70 ± 0.31
Bromochloromethane	2.29 ± 0.01	10.53 ± 0.03	1.97 ± 0.08	11.04 ± 0.26
Dibromomethane	1.88 ± 0.04	8.98 ± 0.13	1.28 ± 0.05	8.71 ± 0.16
Chloroform	3.52 ± 0.07	13.11 ± 0.21	3.39 ± 0.04	14.36 ± 0.12
Dichlorobromomethane	3.44 ± 0.05	12.68 ± 0.15	3.16 ± 0.08	13.52 ± 0.25
Dibromochloromethane	2.99 ± 0.18	10.93 ± 0.56	2.65 ± 0.02	11.68 ± 0.07
Bromoform	3.19 ± 0.10	11.39 ± 0.32	2.97 ± 0.02	12.61 ± 0.06
Carbon tetrachloride	0.70 ± 0.32	7.89 ± 1.01	0.75 ± 0.47	9.71 ± 1.47
Bromotrichloromethane	2.75 ± 0.21	12.21 ± 0.67	2.38 ± 0.18	13.06 ± 0.58
1,1,1-Trichloroethane	1.58 ± 0.27	10.57 ± 0.87	0.79 ± 0.24	9.39 ± 0.76

Table VI. Equilibrium Constants K(l. mol^{-1}) with Di-*n*-octylmethylamine

Solutes	30°	40°	50°	60°
Dichloromethane	0.206	0.181	0.161	0.144
Chlorobromomethane	0.223	0.197	0.176	0.158
Dibromomethane	0.247	0.224	0.204	0.186
Chloroform	0.472	0.392	0.329	0.279
Dichlorobromomethane	0.513	0.428	0.360	0.307
Dibromochloromethane	0.582	0.497	0.428	0.372
Bromoform	0.645	0.544	0.465	0.400
Carbon tetrachloride	0.060	0.058	0.056	0.054
Bromotrichloromethane	0.206	0.178	0.155	0.136
1,1,1-Trichloroethane	0.067	0.062	0.057	0.053

Table VII. Equilibrium Constants K(l. mol^{-1}) with Tri-*n*-hexylamine

Solutes	30°	40°	50°	60°
Dichloromethane	0.093	0.084	0.077	0.071
Chlorobromomethane	0.101	0.091	0.083	0.075
Dibromomethane	0.104	0.098	0.092	0.086
Chloroform	0.203	0.170	0.143	0.122
Dichlorobromomethane	0.212	0.179	0.153	0.132
Dibromochloromethane	0.228	0.198	0.174	0.154
Bromoform	0.241	0.206	0.178	0.155
Carbon tetrachloride	0.026	0.025	0.024	0.023
Bromotrichloromethane	0.073	0.064	0.057	0.051
1,1,1-Trichloroethane	0.033	0.032	0.031	0.029

Discussion

Examination of the equilibrium constants listed in Tables VI and VII reveals trends that show a remarkable similarity to those observed with the thioether systems in ref 1 and provide support for our contention that two types of complexation can exist in these systems, *viz.*, (1) hydrogen bonding of the C–H proton of the haloalkane to the N atom of the amines, (2) charge transfer (n → σ^* type) between the N atom and the halogen atoms of the haloalkane. For example, within the haloform series we observe an *increase* in K as Br atoms replace Cl atoms (proceeding along the series $CHCl_3 \rightarrow CHBr_3$) instead of the *decrease* which we would expect if the K was a direct measure of the hydrogen acidity alone. This indicates that, although the acidity of the hydrogen on the haloform is reduced when a Br replaces a Cl, the increased "charge-transfer" interaction between the N atom and the Br atom more than compensates for the diminished H bonding. This trend is clearly observed for the haloform and the dihalomethane series with both tertiary amines. The smaller absolute values for the dihalomethane K's compared with the haloforms are related both to the lower activity of their C–H hydrogens and the fewer halogen atoms available for nitrogen/halogen interaction. Also note the larger K and $|\Delta H|$ values (Table VIII) for bromotrichloromethane in comparison to 1,1,1-trichloroethane and carbon tetrachloride.

The K values for all the haloalkanes with di-*n*-octylmethylamine (DOMA) are larger than the corresponding systems involving tri-*n*-hexylamine (THA). This, of course, is what one would expect on the basis of steric considerations, the N atom in DOMA being more accessible than the N atom in THA. Thus one might expect these differences in K values to be reflected entirely in the ΔS values for the respective systems. However, inspection of the ΔH and ΔS data in Table VIII reveals that this is not entirely the case. While the ΔS values for the THA systems are generally more negative than those for the respective DOMA systems, the ΔH values for the DOMA systems are also more negative than those involving THA. Thus, it would appear that the difference in K values is a combination of two factors: steric *and* electronic. The more negative ΔS values for the THA systems are indicative of steric hindrance, while the more negative ΔH values for the DOMA systems are indicative of tighter binding in these complexes. These observations lead us to the interesting conclusion that increasing the accessibility of the N atom by reducing the length of one alkane chain to a minimum has the effect not only of increasing the probability of complexation (ΔS effect), but also allows closer approach of the C–H proton for H bonding (or the halogen atom for charge transfer), resulting in a somewhat stronger interaction (ΔH effect).

Given the probable existence of more than one kind of complex in these systems, it becomes very difficult to offer a quantitative interpretation of the experimental association parameters. However, a number of qualitative observations may be made regarding the systems studied here and those in the preceding paper. Examination of the ΔH values in Table VIII here and in Table IX of ref 1 indicates that, in general, the $|\Delta H|$ values follow the trend of donor strength N > O > S with a given acceptor. This is the trend which has been observed in previous studies of H bonding with n donors and conforms to that expected on the basis of electronegativity considerations. However, the trend in $|\Delta S|$ is also observed to be N > O > S; *i.e.*, S, in general, has the least negative ΔS value with a given acceptor. This also might be expected on the basis of the larger S atom being more accessible to the acceptor sites. Thus, N appears to be the better donor ΔH-wise but not ΔS-wise. We also see that $CHCl_3$ has the largest K and $|\Delta H|$ with DOMA, indicative that the strongest H bonding occurs in this system, as expected. However, within the haloform series the $|\Delta H|$ values drop but slightly from $CHCl_3$ through $CHBr_3$ while the ΔS's become less negative resulting in an overall increase in K. This could possibly be explained in terms of an increasing amount of "soft" charge-transfer interaction between the N and Br atoms. The charge-transfer interaction will be relatively weaker than the H-bonding interaction and will occur at relatively longer intermolecular separations, thus being less affected by the steric environment of the N atom.

It is worth noting at this point that, while the interpretations of the measured thermodynamic association constants outlined above may be reasonably valid, in fact thermodynamic data *per se* yield no evidence concerning the presence or absence of weak complexes in a system. Evaluation of the extent of complex formation depends on some kind of plausible molecular model. The information obtained (in this case, equilibrium constants) is only as reliable as the model from which it is deduced. In terms of the molecular model invoked here the equilibrium constants obtained from the glc data represent the fractions of molecules which exist as distinct 1:1 "complexes," whether of the H-bonded type, the charge-transfer type, or both. With regard to evidence from other sources as to the existence of these complexes, we have already pointed out[1] that, in addition to the well-documented evidence for C–H hydrogen bonding to tertiary amines, charge-transfer bands have been observed in solutions containing a tertiary amine together with a variety of halomethanes.[2] Again, the observation of a charge-transfer band does not in itself prove the existence of 1:1 complexes in solution. However, taken together with the values for the association constants obtained from the glc data, it seems, at least for the amine/halomethane systems (if not for the thioether systems), that complexes other than simple H-bonded ones are found in these solutions and that charge-transfer forces are responsible for at least part of their stabilization.

It would, of course, be of great interest to pursue further studies of these systems (*e.g.*, by spectroscopic techniques) in an effort to resolve the "mixed" association constants into the individual contributions from the different types of complexes. Despite the well-known difficulties involved with the extraction of accurate thermodynamic parameters for weak intermolecular complexes from spectroscopic data, it seems likely that at least the hydrogen-bonding contribution could be evaluated fairly accurately by a careful spectroscopic study. This question will be addressed in more detail in a subsequent publication.[8]

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(8) Paper VI in this series: J. P. Sheridan, D. E. Martire, and S. E. O'Donnell, *J. Amer. Chem. Soc.*, submitted for publication.

Radical Stabilization Energies in Esters. The α-Carbomethoxy Group from Kinetics of the Thermal Isomerization of 1-Chloro-4-carbomethoxybicyclo[2.2.0]hexane in the Liquid Phase

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Abstract: The thermal isomerization of 1-chloro-4-carbomethoxybicyclo[2.2.0]hexane has been studied in the liquid phase over the temperature range 76–137°. Good first-order kinetics were obtained and the rate constants were well represented by the Arrhenius equations $\log (k_a/\text{sec}^{-1}) = (13.65 \pm 0.07) - (30.16 \pm 0.12)/\theta$, $\log (k_b/\text{sec}^{-1}) = (13.58 \pm 0.12) - (30.00 \pm 0.21)/\theta$, and $\log (k_c/\text{sec}^{-1}) = (13.08 \pm 0.26) - (29.14 \pm 0.45)/\theta$, where $\theta = 2.303RT$ kcal/mol, the error limits are the least-squares deviations, and the subscripts a, b, and c refer respectively to nitrobenzene, diphenyl ether, and tetrachloroethylene as solvent. From these Arrhenius parameters and transition state estimates for a biradical mechanism, the radical stabilization energy of an α-carbomethoxy group is shown to be 4.0 ± 1.7 kcal/mol relative to a hydrogen atom. This is in excellent agreement with a stabilization energy of 4.0 ± 1.9 kcal/mol that we have derived from a single rate of isomerization of 1,4-dicarbomethoxybicyclo[2.2.0]hexane measured independently of this work. The magnitude of this stabilization energy is discussed in terms of polarity effects in radical structures for esters and ketones as strong evidence for a biradical intermediate in the thermal isomerization of bicyclo[2.2.0]hexanes.

An understanding of free-radical chemistry is greatly facilitated by the use of the concept of stabilization (or resonance) energies. By the use of stabilization energies and appropriate standard models, it has been possible to test the self-consistency of the kinetic parameters for a wide variety of free-radical reactions.[2]

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