Voraussetzung für die statistisch-mechanische Behandlung von „Übergangszuständen" nach der Eyring-Theorie. Man darf deshalb den Schluß aus unseren Ergebnissen ziehen, daß die Theorie vom Übergangszustand unterhalb 1 eV tatsächlich anwendbar ist, mit Ausnahme einiger einfacher Systeme, wie das erwähnte System $Ar^+ + D_2$.

Bei einer Energie des einfallenden Ions von 40 eV befindet man sich gerade im Übergangsbereich zwischen dem Stripping- und Komplex-Mechanismus für die Reaktion nach Gl. (5) (Abb. 3). Die Geschwindigkeit des Ions beträgt hier $1{,}6 \cdot 10^6$ cm·sec^{-1}. Nimmt man an, daß die Wechselwirkung mit der D_2-Targetmolekel im wesentlichen über einen Abstand von 3 Å erfolgt, errechnet sich eine Stoßzeit von $2 \cdot 10^{-14}$ sec. Diese Zeit mag als rohe Abschätzung der Zeit zur Relaxation der überschüssigen Energie zwischen dem kritischen und den übrigen Freiheitsgraden der reagierenden Teilchen (im wesentlichen des vielatomigen Ions) gelten. Für die Reaktion zwischen dem Molekel-Ion und der CD_4-Molekel, bei der die relative kinetische Energie bei gleicher Geschwindigkeit viel größer ist als bei der Reaktion mit D_2 (und entsprechend der Betrag der zu verteilenden Energie), entnimmt man aus Abb. 1 eine Übertragungsenergie von ca. 4 eV des Ions im Laborsystem. Die Zeit zur Relaxation wird unter diesen Umständen etwa $6 \cdot 10^{-14}$ sec. Jedenfalls zeigen diese einfachen Abschätzungen, daß in vielatomigen Reaktionspartnern die Zeit zur Verteilung der Schwingungsenergie auf die verschiedenen Freiheitsgrade etwas kleiner oder etwa gleich der Zeit ist, die für eine Schwingungsperiode in den beteiligten Freiheitsgraden benötigt wird.

Der Deutschen Forschungsgemeinschaft danken wir für die Unterstützung dieser Untersuchungen. Einer von uns (D. H.) ist der Firma CIBA für die Gewährung eines Stipendiums sehr zu Dank verbunden.

Temperature and Solvent Dependence of $^{13}C-H$ Spin-Spin Coupling Constant J_{CH} in Ethyl Formate

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(Z. Naturforsch. **23 a**, 2094—2097 [1968]; received 20 September 1968)

PMR spectra of pure ethyl formate and its solutions in carbon tetrachloride, carbon disulfide and acetone indicate that both the directly bonded $^{13}C-H$ coupling constant and the chemical shift of the formyl group vary with temperature, solvent and concentration. Some aspects of the temperature and solvent dependence of J_{CH} and δ can be related to the intermolecular hydrogen bonding involving the formyl proton. The possibility of the existence of other factors must however not be forgotten.

The temperature and solvent effects on the $^{13}C-H$ coupling constant have been studied by many authors [1–8]. However, there is no adequate theory to explain these effects.

LASZLO [4] has pointed out that the temperature dependence of J_{CH} could be explained by a combination of intramolecular and intermolecular effects. The former could be the excitation of different vibrational states in the C – H bond, and the latter dispersion forces and self-association.

According to EVANS [1], there is a qualitative relation between the increase in J_{CH} of chloroform and the proton acceptor strength of the solvent molecules. The experimental results of DOUGLAS and DIETZ [6] are in accordance with the Evans' hypothese. Some investigators [9] have pointed out that the sol-

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vent mechanism is the polarization through electric fields created by neighbouring molecules.

Coupling constants J_{CH} for a series of compounds containing the formyl group have been measured by MULLER [10]. He has considered the influence of different molecular parameters as hybridisation, bond length, and polarity of the C – H bond, on J_{CH}. Recently HAYAMIZU and YAMAMOTO [11] studied ethyl formate in the solvents CCl_4, CS_2, CH_3OH, and C_6H_6 but did not find any significant changes of the long range proton – proton coupling constants.

In this work the temperature and solvent dependence of the $^{13}C-H$ coupling constant and the proton chemical shifts of the formyl group in pure ethyl formate and its solutions in carbon tetrachloride, carbon disulfide and acetone will be reported.

Experimental

The ethyl formate, carbon disulfide and carbon tetrachloride used, were commercially available products and the PMR spectra showed no traces of impurities. Acetone was dried over molecular sieves and finally distilled. Samples were prepared in dry nitrogen by weighing solute and solvent into a PMR sample tube, and adding a small amount of tetramethylsilane (TMS) to serve as internal calibration reference. Samples were frozen in liquid nitrogen and thereafter sealed with a hot flame. The accuracy of concentrations was ±1 mole per cent. The spectra were recorded with a Varian Associates A-60 spectrometer operating at 60 MHz. Sample temperatures were regulated by a Varian V-6040 temperature controller and measured with Varian-supplied calibration samples. Temperatures are accurate to ±3 °C. Calibrations were performed by the common sideband technique, using a variable frequency audio oscillator Hewlett-Packard 241 A constantly monitored by an Advance model TC 4 counter. The values of J_{CH} are averages of 3 – 5 scans in both sweep directions and are accurate to ±0.2 Hz. The accuracy of chemical shifts is ±0.5 Hz.

Results

The values of the coupling constant J_{CH} of the formyl group of ethyl formate at different temperatures are presented in Table 1. Shown in this Table are also the values of the chemical shift of the formyl proton, measured at the same temperatures, relative to the methyl protons of ethyl formate and to internal TMS. The variation of J_{CH} and δ with temperature can be seen in Fig. 1. The relationship between J_{CH} and δ in pure ethyl formate can be found in Fig. 2. In the relatively concentrated solutions studied, as for instance in pure liquid, the lowering of temperature increases both the coupling constant J_{CH} and the chemical shifts δ and δ_{TMS} as shown in Tables 2 and 3.

It can clearly be seen that both J_{CH} and δ decrease with dilution in carbon disulfide and carbon tetrachloride at each temperature. In acetone solu-

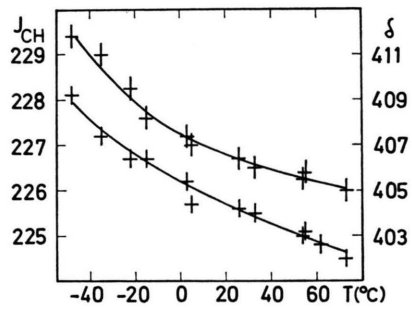

Fig. 1. Coupling constant J_{CH} and chemical shift δ of ethyl formate as a function of temperature. The lower curve shows the variation of J_{CH} and the upper the variation of the chemical shift δ between the formyl and methyl protons.

T °C	J_{CH} Hz	δ[a] Hz	δ^{b}_{TMS} Hz
+ 73	224.5	405.0	480.2
+ 61	224.8	—	—
+ 55	225.1	405.4	480.8
+ 54	225.0	405.5	481.0
+ 33	225.5[c]	406.0	481.2[d]
+ 26	225.6	406.4	481.9
+ 5	225.7	407.0	482.4
+ 3	226.2	407.4	483.5
− 15	226.7	408.2	485.0
− 22	226.7	409.5	485.0
− 35	227.2	411.0	487.0
− 48	228.1	411.8	489.0

[a] Chemical shift of the formyl proton relative to the methyl protons of ethyl formate.

[b] Chemical shift of the formyl proton relative to internal TMS.

[c] MALINOWSKI et al. [12] have measured J_{CH} = 225.6 Hz from the PMR spectrum at room temperature.

[d] HAYAMIZU and YAMAMOTO [11] have found δ_{TMS} = 8.021 ppm = (5/3) · 481.3 Hz using a 100 MHz spectrometer at room temperature.

Table 1. Coupling constant J_{CH} and proton chemical shifts of formyl group for pure ethyl formate at different temperatures.

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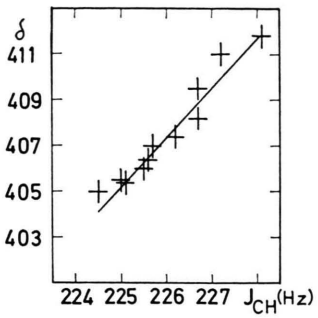

Fig. 2. The chemical shift δ versus J_{CH} for pure ethyl formate.

T °C	C mole%	J_{CH} Hz carbon disulfide	δ Hz carbon disulfide	J_{CH} Hz carbon tetrachloride	δ Hz carbon tetrachloride
+86	60	—	—	224.4	400.8
	40	—	—	223.9	398.8
	20	—	—	223.7	398.2
+54	60	224.5	402.4	224.5	402.2
	40	224.3	401.0	224.3	400.5
	20	224.2	398.5	223.9	399.8
+26	60	225.1	403.4	224.9	402.6
	40	224.6	400.6	224.6	400.0
	20	224.2	399.2	224.6	400.0
+ 3	60	225.9	405.5	225.9	405.0
	40	225.4	403.0	225.2	402.0
	20	225.0	400.5	225.0	401.0
−15	60	226.0	406.2	226.2	404.8
	40	225.7	403.4	225.6	403.8
	20	225.1	401.2	225.3	402.2
−48	60	227.5	409.0	—	—
	40	227.3	407.0	—	—
	20	226.5	403.8	—	—

Table 2. Coupling constant J_{CH} and chemical shift δ of ethyl formate in solutions of carbon disulfide and carbon tetrachloride at different temperatures.

tions the variation of J_{CH} with concentration is much less and apparently goes in opposite direction as compared to the case when unpolar solvents were used, whereas δ clearly increases with dilution in acetone.

Discussion

The data presented in Table 1 show that when the temperature of pure ethyl formate decreases by 120°, the total increase in J_{CH} is 3.6 Hz. In recent literature [2, 4, 6] an approximately equal increase of J_{CH} with the decrease of temperature for different compounds has been reported. Thus the phenomenon could be at least partially connected with intermolecular association, which increases with decreasing temperature. The same explanation is probably also valid for ethyl formate, which probably is an associated substance [10, 13]. The observed low field shift of the formyl proton with decreasing temperature, both in pure ethyl formate and in its CCl_4 and CS_2 solutions, is in the same direction as the normal hydrogen bond shift, and thus supports the self-association which is assumed to occur through the CHO proton.

T °C	C mole%	J_{CH} Hz	δ Hz	δ_{TMS} Hz
+73	60	224.6	406.0	481.0
	39	224.6	406.0	480.6
	25	224.7	407.0	481.4
	11	—	407.4	482.2
+55	60	225.1	406.6	481.6
	39	225.2	407.0	481.8
	25	225.2	408.6	483.2
	11	—	408.7	483.1
+33	60	225.5	407.0	481.5
	39	225.6	408.4	483.2
	25	225.6	409.2	483.6
	11	—	409.6	484.3
+ 5	60	225.8	409.6	484.8
	39	225.8	411.0	486.2
	25	226.1	411.6	486.5
	11	—	412.2	487.2
−22	60	226.7	411.0	486.5
	39	226.8	412.2	487.6
	25	226.8	412.6	488.0
	11	—	414.3	489.2
−35	60	227.3	412.5	488.4
	39	227.4	413.2	489.0
	25	227.4	414.0	489.2
	11	—	415.0	490.2

Table 3. Coupling constant J_{CH} and chemical shifts of ethyl formate in acetone at different temperatures.

T °C	$\Delta J^{a}_{CCl_4}$ Hz	$\Delta J^{a}_{CS_2}$ Hz	T °C	$\Delta J^{b}_{(CH_3)_2CO}$ Hz
+54	−1.1	−0.8	+73	+0.2
+26	−1.0	−1.4	+55	+0.1
+ 3	−1.2	−1.2	+33	+0.1
−15	−1.4	−1.6	+ 5	+0.4
−48	—	−1.6	−22	+0.1
—	—	—	−35	+0.2

[a] $\Delta J = J$(20% in CCl_4 or CS_2) $- J$(pure).
[b] $\Delta J = J$(25% in $(CH_3)_2CO$) $- J$(pure).

Table 4. Solvent induced changes of J_{CH} at different temperatures. ΔJ's are accurate to ± 0.4 Hz.

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Table 4 gives additional support to the assumption that the participation of the formyl proton in the hydrogen bond C – H···O increases J_{CH}. When ethyl formate is diluted with CCl_4 or CS_2 in a mole ratio 1 : 4, J_{CH} is lowered by more than 1 Hz. Apparently now the decrease of J_{CH} as well as the decrease of the expressions $|(\Delta J/\Delta T)_{+30°}|$ and $|(\Delta\delta/\Delta T)_{+30°}|$, are due to the decrease of the number of the molecules participating in the H-bond. MULLER [10] proposed that when the carbonyl oxygen of the formyl group participates in the hydrogen bond the effective electronegativity of carbon and consequently also J_{CH} would increase. This could also explain partially the observed decrease of J_{CH}, is it that the self-association occurs through the alcoxyl oxygen or the carbonyl oxygen. In this case it is difficult to interpret the observed changes as a result of dispersion interactions only [14]. In these two solvents $|\Delta J|$ seems to attain the greatest values at the lowest temperatures studied (Table 4), which is to be expected, bearing in mind that hydrogen bonding is the stronger the lower the temperature, and that an inactive unpolar solvent breaks relatively more bonds the lower the temperature is.

In the acetone solutions J_{CH} is only slightly greater than in pure ethyl formate. Since the dilution with acetone does not produce a similar decrease of J_{CH} as that with inert solvents, evidently disengaging molecules from ethyl formate – ethyl formate complexes are combined into ethyl formate – acetone complexes. The localized electric field effects produced by the active parts in the ethyl formate and acetone molecules – the dipolar C = O groups – are of equal magnitude in both cases. In this case no marked growth in J_{CH} was observed although e. g. EVANS [1] has measured such an effect for chloroform in acetone. This situation apparently is due to the above mentioned electric effects in addition to the fact that the self-association in chloroform is weaker than in formates. The increase of the chemical shift of the formyl proton and also that of the expression $|(\Delta\delta/\Delta T)_{+30°}|$ from $5\cdot10^{-4}$ to $11\cdot10^{-4}$ ppm/°C when going from 100 to 11 mole per cent concentration support the formation of ethyl formate – acetone complexes predominantly with increasing dilution.

The relationship between J_{CH} and δ both in pure ethyl formate and the solutions studied seems to be linear. This has been interpreted [5, 7, 15] to indicate the equivalence of the mechanisms affecting J_{CH} and δ. When plotting J_{CH} against δ, measured at the same temperature for different concentrations, the slopes of the graphs for unpolar CCl_4 and CS_2 are found to be clearly different from that for polar acetone. WATTS et al. [8] have reported that for dichloroethylenes the corresponding slope changes in the same sense, when passing from cyclohexane to polar dimethylformamide as solvent.

The observed changes of J_{CH} and δ have in the foregoing been interpreted through intermolecular H-bonding and electric interactions between the molecules. However, one must bear in mind that for instance the temperature dependence of the intramolecular excitation of stretching and bending vibrations in the C – H bond, should also be taken into account [16, 4].

The authors wish to thank Prof. P. TUOMIKOSKI for most valuable discussions. We are also grateful to Dr. P. TANSKANEN for revising the English language of the manuscript. This work was supported by the National Research Council for Sciences. One of us (E. R.) is also indebted to Neste Oy for financial support.

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