Solvent Extraction Studies by the AKUFVE Method

IV. Spectrophotometric Determination of the Distribution of Acetylacetone

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Using the AKUFVE method with spectrophotometric detection, the distribution of acetylacetone between different organic solvents and aqueous sodium perchlorate was investigated. It was found that the distribution constant \( k_d \) decreased with increasing ionic strength for the organic solvents benzene, toluene, xylene, mesitylene, ethyl benzene, and chloroform. At constant ionic strength, \( k_d \) decreased with increasing number of methyl groups in substituted benzene. Furthermore, \( k_d \) decreased with increasing temperature for the chloroform system, but remained nearly constant in the other systems. The results are discussed in relation to NMR measurements, and calculated \( \Delta H \) and \( \Delta S \) values.

Using the newly developed AKUFVE technique\(^4\), we have for some time in our laboratory determined thermodynamic constants for the formation and distribution of metal complexes between organic and aqueous solutions.\(^4\) For these determinations it is necessary to know the distribution constant \( k_d \) of the complexing agent itself between the two liquid phases as a function of temperature, ionic strength and pH. In the present paper, the results for acetylacetone (HAA) are reported, using spectrophotometric determinations in both phases. This method of detection has been adopted to the AKUFVE technique to provide fast and continuous measurements. The apparatus is shown in Fig. 1.

SPECTROPHOTOMETRIC DETERMINATION OF \( k_d \)

The distribution constant \( k_d \) may be defined as

\[
k_d = \frac{[\text{HAA}]_{\text{org}}}{[\text{HAA}]_{\text{aq}}}
\]

(1)

Acta Chem. Scand. 23 (1969) No. 8
Fig. 1. The AKUFVE system for spectrophotometric detection. A and O are the aqueous and organic phase connections, respectively. I's are inspection glasses. V₁, V₂, and V₃ are valves for regulating the three main liquid flows. V₄ and V₅ are three-way stopcocks for regulating the side-streams to the detection units.

where [ ] means concentration, "org" refers to the organic phase and "aq" to the aqueous phase. In the spectrophotometric analysis the relationship

\[ A = c \cdot \varepsilon \cdot d \]  \hspace{2cm} (2)

is valid, where $A$ is the absorbance, $c$ the concentration of the substance (M),
$\varepsilon$ its molar extinction coefficient (M$^{-1}$ cm$^{-1}$) and $d$ the thickness of the cell (cm).
Combining these equations one obtains

$$k_d = \frac{A_{org} \cdot \varepsilon_{aq}}{A_{aq} \varepsilon_{org}} \cdot \frac{d_{aq}}{d_{org}}$$

(3)

$\varepsilon$ depends on ionic strength ($I$), pH and temperature ($T$). In order to
determine $k_d(I, pH, T)$ calibration curves for the absorbance of HAA in the
organic solvents and in the sodium perchlorate solutions must be obtained,
and the corresponding $\varepsilon$-values be computed, before eqn. 3 can be applied
for the calculation of $k_d$. In order to extend the measurable concentration
region it is practical to use different cell length in the two phases.

**EXPERIMENTAL**

*Chemicals.* The acetylacetone was of pract. quality (Fluka); it was purified according
to Rydberg. The sodium perchlorate solutions were made by titration of concentrated
HClO$_4$ (Merk p.a.) with 10 M NaOH (pH-Tamm). Benzene, toluene, xylene, cyclo-
hexane, hexane, carbon tetrachloride, chloroform, and methylene chloride, were all p.a.
(Merk). Gas chromatographic analysis showed that the xylene consisted of about 3 %
pr., 83 % m-, and 14 % o-xylene. Mesitylene and ethyl benzene were *puriss.* (Fluka).

*Selection of wavelengths.* Acetylacetone has an absorption maximum at 273.5 nm in
sodium perchlorate solutions. In the organic solvents used the maximum occurs between
270 and 273.5 nm. Normally the absorbance was measured at the absorption maximum.
This was done for all solvents but benzene and its homologues and kerosene. These
solvents absorb to a certain extent at 273 nm. Because the solubility of these solvents

*Fig. 2.* Spectrum of (a) acetylacetone in 1 M NaClO$_4$ + 0.001 M HClO$_4$, (b) 1 M
NaClO$_4$+0.001 HClO$_4$ saturated with toluene at 5°C, and (c) same as (b) but
at 40°C. The arrows indicate the wavelength chosen for quantitative determination
of acetylacetone in the presence of toluene.

in sodium perchlorate varied with temperature and ionic strength it was necessary to measure the absorbance on the slope of the acetylacetone absorption peak, where the influence from the solvents was almost negligible (Fig. 2). Wavelengths chosen for the different systems are listed in Table 1.

After calibration curves for a system had been obtained, the spectrophotometer settings were not changed at any time until all experiments on the system had been finished. This is particularly important for measurements made on the slope of an absorption peak.

**Apparatus.** In the AKUFVE system (Fig. 1) equal volumes of organic and aqueous phases are brought into contact in a mixing chamber, from which the mixture flows down into the centrifuge, in which absolute phase separation takes place. The pure light and heavy phases pass through identical arrangements. The main fraction of each phase flows through a flow meter and a heat exchanger back into the mixer. The heat exchanger and the cooling jacket around the centrifuge are connected to a thermostat, which removes the heat developed in the centrifuge. The thermostat can either be used to keep the temperature constant, or to allow the temperature to rise slowly during a run. A very accurate thermometer is placed in the mixer.

During an AKUFVE run different parameters can be changed, e.g. concentration of complexing agent, ionic strength, pH, and temperature. When starting a run, equal volumes of organic and aqueous phases (about 300 ml each) are introduced to the mixer, air pressure is applied to the centrifuge motor, the stirrer is started, and the valve \( V_1 \) between mixer and centrifuge opened. Both phases leaving the centrifuge must be clear and free from air bubbles, which can be accomplished by adjusting the throttling valves \( V_1 \) and \( V_2 \) if necessary. The temperature of the system is set on the desired value with the thermostat 1, and the temperature in the detection unit is set a few degrees higher with the thermostat 2. The three-way stopcocks \( V_3 \) and \( V_4 \) can now be opened enough to give the proper flow rate over the pre-heater to the cell compartments of the spectrophotometers, which are connected to the same thermostat. The cell compartments contain a reference cell and a flow-through cell from which the solution flows back to the mixer via inspection glasses where the flow rates can be checked.

The two phases leaving the centrifuge are saturated with respect to each other. If the temperature in the measuring part becomes lower than the temperature in mixer and centrifuge, oversaturation occurs, and droplets of the dissolved phase will precipitate in the previously clear phase. This would make spectrophotometric detection impossible. It is therefore necessary to keep the detection arrangement at a slightly higher temperature than mixer and centrifuge.

Two Metrohm burettes containing \( \text{NaClO}_4 \) and \( \text{HClO}_4 \) are connected to the mixer. The emf in the aqueous phase is measured with a glass electrode in the side-stream, where the flow rate is slow enough to avoid disturbances in the measurement.\(^4\) When the aqueous phase is the lighter one it is necessary to interchange the phase output connections on the centrifuge.

The centrifuge is made of titanium. Tube connections, valves and some parts in the mixer are made of stainless steel. The three-way stopcocks, pH-cell, mixer top and bottom, and all tubes are made of teflon. Heat exchangers, mixer walls, flowmeters and flow-through cells are made of glass. The centrifuge is driven by an air compression motor, which gives the centrifuge bowl a rotation speed of up to 18 000 rpm.

The absorption measurements are made with Beckman double beam spectrophotometers. For simultaneous registration of both phases, two such spectrometers are used, connected to a Beckman 10-inch recorder via a cam wheel switch, which provides recording in 30 sec intervals alternating between the two spectrometers.

**AKUFVE RUNS**

At high pH-values, acetylacetone dissociates \( \left( k_a = 10^{-8.9} \right) \). The \( \text{AA}^- \) ion absorbs stronger than undissociated HAA; the maximum value of \( \varepsilon \) for \( \text{AA}^- \) occurs at 290 nm, and is about 14 times higher than for undissociated HAA. Even at 273.5 nm, where HAA has its \( \varepsilon \)-maximum in aqueous solution, the

e-value of AA⁻ is about 7 times that of undissociated HAA. It is therefore necessary to make all distribution measurements of HAA in slightly acidic solutions (pH < 6) in order to avoid interference from AA⁻ in the spectrophotometric measurements.

When the AKUFVE apparatus works properly, i.e. the temperature is the desired one and two absolutely pure phases pass through the detection cells, the recorder is started and gives zero values of the absorbances of both phases, indicated by \( A_{org}^0 \) and \( A_{aq}^0 \) in Fig. 3. This registration is continued for some time, until constant \( A^0 \) values are reached. After changing the conditions in the system, as HAA concentration, ionic strength or temperature, new absorbance values \( A_{org}' \) and \( A_{aq}' \) are obtained, see Fig. 3. Because the corresponding e-values are known from calibration runs, \( k_d \) can be calculated from these measured values, using eqn. 3, where \( A_{org} = A_{org}' - A_{org}^0 \), and \( A_{aq} = A_{aq}' - A_{aq}^0 \). Further changes give \( A_{org}'' \) and \( A_{aq}'' \), etc.

\[ \text{HAA-concentration dependence.} \]

When the \( k_d \) dependence on the concentration of HAA was to be studied at a certain ionic strength, pH, and temperature, the \( A_{org}^0 \) and \( A_{aq}^0 \) were recorded and a small volume (0.2—2.0 ml) of 0.1 M HAA in the organic solvent was then added to the mixer. The absorbance was continuously recorded, reaching the equilibrium values indicated \( A_{org}' \) and \( A_{aq}' \) in Fig. 3.

By successive additions of HAA, a series of \( A_{org} \) and \( A_{aq} \) values was obtained, from which \( k_d \) was computed as described above. The HAA concentration was increased in this way until one of the phases had reached an absorbance close to 2.0.

If \( k_d \) is independent of [HAA] (see below), \( k_d \) can be calculated in 6 different ways after 3 HAA additions, and in \( \frac{1}{2} n(n+1) \) ways after \( n \) additions. This improves the reliability of the calculated \( k_d \)-values.

Ionic strength dependence. When the dependence of $k_d$ on the ionic strength ($I$) was to be studied at constant pH and temperature, this was done by adding a very concentrated NaClO₄ solution to the mixer which contained 0.001 M HClO₄ as aqueous phase from the beginning. Due to the limited volume of the mixer, an $I$-value of 1.0 could not be achieved in this way. Therefore AKUFVE runs were normally done at different but constant ionic strengths, while other parameters like concentration of HAA or temperature were varied.

Temperature dependence. When the temperature dependence of $k_d$ was studied, the run was started up as described earlier, but the two thermostats were adjusted to different temperatures before the $A^0$ absorbances were recorded. Thermostat 1, which was connected to mixer and centrifuge, was set on a value slightly lower than the temperature wanted in the mixer. The difference in temperature between mixer and thermostat was about 2 degrees at room temperature and about 5 degrees at 10°C in the mixer. Thermostat 2, which was connected to the detection units, was set at the highest temperature that was to be reached in the mixer during the run, thus eliminating variations in the $ε$-value during the experiment.

When the temperatures in the mixer and the cells became constant, the zero absorbances were recorded for about half an hour to see that $A_{org}^0$ and $A_{aq}^0$ were constant. Then a proper amount of HAA was added to the mixer. When it was seen on the recorder that equilibrium had been reached, the temperature of mixer and centrifuge was slowly raised. This was best done by switching off thermostat 1, so that only the pump worked. The heat developed in the centrifuge then was enough to raise the temperature slowly in the mixer. This temperature rise could be varied by changing the volume of the water in the thermostat, or by changing the speed of the centrifuge. Usually a rise of 1 degree per 10—15 min occurred.

There were some limitations to this technique. At temperatures over 45°C, small air bubbles were formed in the detection cells after some time. In the flow-through cells they were removed with the liquid flow, which went upwards through the cell, but in the reference cell the bubbles stuck to the cell walls and changed the absorbance.

The flow rate in the side-stream always had to be so slow, that the liquid reached the detection cell with the right temperature. With a temperature difference of 25°C between mixer and detection cell, the delay was about 2 min, but with a temperature difference of 10°C, it was possible to increase the flow rate to give a delay of only 30 sec.

Experiments made by ordinary shaking technique. When the ionic strength was chosen to be 1 M, it was not possible to reach pH-values below 1 by adding 1 M HClO₄ because of the limited liquid volume of the AKUFVE system. When studying the dependence of $k_d$ at high acidities (Table 2), it was therefore necessary to complement the AKUFVE runs by experiments using manual shaking technique: A lot of glass ampoules with equal amount of organic and aqueous phase, with HAA, and with pH between 0 and 3, and $I = 1$ M (NaClO₄), were shaken in a thermostated room for 2 h. Then the phases were separated, centrifuged, and analysed spectrophotometrically for HAA. Because the absorbance depended on pH at pH$<3$, calibration curves for each pH had to be made in advance.

Similar experiments were also made with 0.001 M HClO₄ and several other organic solvents (Table 1).

RESULTS

For ionic strength between 0.001 and 1 M, $k_d$ was found to be independent of the HAA concentration in the measured concentration range, 0.03—3 mM, for all solvent systems studied. Higher concentrations could not be directly measured spectrophotometrically because of the high absorbancy. The $k_d$ values in 0.001 M HClO₄ are listed in Table 1.

The dependence of $k_d$ on ionic strength is shown in Fig. 4. For the organic solvents benzene and chloroform $k_d$ was measured both as a function of acidity and ionic strength in the concentration region 0.001—1 M (Table 2). It is obvious that the cation had a considerable influence on the distribution

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Table 1. Wavelengths chosen for the different systems and the measured $k_d$ values at 25°C using 0.001 M HClO$_4$. Manual experiments are marked a; otherwise the AKUFVE technique was used. When the absorbance was measured on the maximum this is marked b.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$\lambda_{\text{org}}$ nm</th>
<th>$\lambda_{\text{aq}}$ nm</th>
<th>$k_d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>278</td>
<td>278</td>
<td>$5.93 \pm 0.02$</td>
</tr>
<tr>
<td>Toluene</td>
<td>284</td>
<td>284</td>
<td>$4.57 \pm 0.02$</td>
</tr>
<tr>
<td>Xylene</td>
<td>288</td>
<td>288</td>
<td>$3.69 \pm 0.01$</td>
</tr>
<tr>
<td>Mesitylene</td>
<td>290</td>
<td>290</td>
<td>$2.73 \pm 0.02$</td>
</tr>
<tr>
<td>Ethyl benzene</td>
<td>286</td>
<td>286</td>
<td>$3.31 \pm 0.02$</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>270.5</td>
<td>273.5</td>
<td>$1.03 \pm 0.01$</td>
</tr>
<tr>
<td>Hexane</td>
<td>270</td>
<td>273.5</td>
<td>$0.95 \pm 0.01$</td>
</tr>
<tr>
<td>Kerosene</td>
<td>290</td>
<td>290</td>
<td>$1.00 \pm 0.01$</td>
</tr>
<tr>
<td>Carbon tetrahloride</td>
<td>272.5</td>
<td>273.5</td>
<td>$3.31 \pm 0.01$</td>
</tr>
<tr>
<td>Chloroform</td>
<td>273.5</td>
<td>273.5</td>
<td>$23.80 \pm 0.30$</td>
</tr>
<tr>
<td>Methylene chloride</td>
<td>273</td>
<td>273.5</td>
<td>$22.50 \pm 0.00$</td>
</tr>
</tbody>
</table>

Table 2. $k_d$ for HAA in the chloroform-water and benzene-water systems at various $I$ (NaClO$_4$ + HClO$_4$) and pH(HClO$_4$) at 25°C. Manual experiments are marked a; otherwise the AKUFVE-technique was used.

<table>
<thead>
<tr>
<th>[H$^+$]</th>
<th>Organic solvent: CHCl$_3$</th>
<th>Organic solvent: C$_2$H$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>$I = 0.001$</td>
<td>$I = 0.1$</td>
</tr>
<tr>
<td>0.001</td>
<td>23.8 ± 0.3</td>
<td>23.3 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>(23.5)$^7$</td>
<td></td>
</tr>
<tr>
<td>0.1</td>
<td>—</td>
<td>20.7 ± 0.4$^a$</td>
</tr>
<tr>
<td>1</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

constant. Fig. 4 also shows the dependence of $k_d$ on acidity for benzene and chloroform. The results agree closely with those found by Rydberg $^5$, Rudenko and Stary,$^6$ Salvinien and Garrigues,$^8$ Peshkova and Peng-Ang,$^10$ and fairly well with values obtained by Wakahayashi et al.$^{11}$

The temperature dependence was studied for systems with benzene, toluene, xylene, mesitylene, ethyl benzene, and chloroform as organic phase and sodium perchlorate solutions of different ionic strength as aqueous phase, buffered to pH 3 with HClO$_4$. For the benzene, toluene, xylene, mesitylene and ethyl benzene systems no marked dependence of temperature was found between $+20$ and $+40$°C.

$k_d$ for the CHCl$_3$ system, however, decreased with increasing temperature as is seen from Fig. 5, where log $k_d$ is plotted as a function of $T^{-1}$. The filled symbols indicate three consecutive runs on the AKUFVE, starting at 15°C.

and ending at 35°C. The circles are values from AKUFVE runs at constant temperature, where other parameters were varied. The large scatter is due to the very low absorbance in the aqueous phase (1 cm cell length), while the absorbance was very high in the organic phase (0.1 cm cell length). The difference between runs 1 and 2 might have been due to a systematic error. It is still small compared with errors commonly obtained by conventional technique, and can probably be further decreased. The reason for the S-formed shape of run 3 is unknown.

By use of a least squares computer program considering all points, the heavy line was obtained. With the well known relationship

$$\log k_d = -\frac{\Delta H}{RT \ln 10} + \frac{\Delta S}{R \ln 10}$$  \hspace{1cm} (4)$$

the slope of the heavy line in Fig. 5 gives $\Delta H = -2.62 \pm 0.16$ kcal·mole$^{-1}$ and $\Delta S = -2.93 \pm 0.19$ cal·mole$^{-1}$ (e.u.).

For CH$_2$Cl$_2$ $k_d$ was also found to be temperature dependent, though to a less extent than for CHCl$_3$ ($k_d \approx 20$ at 3°C, and 16 at 25°C). No temperature dependence was found with CCl$_4$ ($k_d \approx 2.9$ at 3–25°C).
DISCUSSION

From Table 1 it can be seen that the distribution constant $k_d$ decreases with decreasing aromatic and increasing aliphatic character of the organic solvent. This is clearly demonstrated in Fig. 6, where $k_d$ is plotted against the number of methyl groups in substituted benzene, $C_{6}H_{6-n}(CH_{3})_{n}$.

![Fig. 6](image)

**Fig. 6.** Change in $k_d$ with increasing number of methyl groups $(n)$ in substituted benzene, $C_{6}H_{6-n}(CH_{3})_{n}$, at $25^\circ$C and at $I = 0.001$ in (a), 0.1 in (b), and 1.0 M in (c).

In all two-phase systems investigated by us, $k_d$ decreased with increasing ionic strength and acidity of the aqueous phase (Fig. 4). This is in line with the increasing solubility of HAA in salted and acid aqueous solutions, see Table 3.

**Table 3.** Solubility in g/100 ml of acetylacetone in aqueous solutions of various ionic strength and acidity at $25^\circ$C.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>0 M</th>
<th>1 M</th>
<th>2.5 M</th>
<th>5 M</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaClO$_4$</td>
<td>19.2</td>
<td>35.6</td>
<td>55</td>
<td>∞</td>
</tr>
<tr>
<td>HClO$_4$</td>
<td>19.2</td>
<td>48.8</td>
<td>∞</td>
<td>∞</td>
</tr>
</tbody>
</table>

The $k_d$ values in Table 1 can be roughly divided into three groups, with values around 1 (hexane, kerosene, and cyclohexane), 3—6 (in increasing order mesitylene, carbon tetrachloride, ethyl benzene, xylene, toluene, and benzene), and around 23 (methylene chloride and chloroform). For the first group the dielectric constants are $\leq 2$, for the second group 2.2—2.4, and for the third group 5—9. Because acetylacetone is polar (dielectric constant 25) one expects it to interact with other polar solvents, and accordingly be more easily dissolved in them, as Table 1 indicates.

Table 4. NMR measurements on pure acetylacetone, and pure organic solvents, and solutions containing 20 % acetylacetone in these solvents.

<table>
<thead>
<tr>
<th>Solution at 32°C</th>
<th>Enol %</th>
<th>Keto %</th>
<th>H in enol OH, cps</th>
<th>H in solvent, cps</th>
<th>Ratio $-\text{OH}/-\text{CH}=$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HAA</td>
<td>75</td>
<td>25</td>
<td>924</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>HAA in CCl₄</td>
<td>93</td>
<td>7</td>
<td>915</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>CHCl₃</td>
<td>83</td>
<td>17</td>
<td>825</td>
<td>436</td>
<td>0.5</td>
</tr>
<tr>
<td>HAA in CHCl₃</td>
<td>66</td>
<td>34</td>
<td>812</td>
<td>445</td>
<td>0.8</td>
</tr>
<tr>
<td>CH₃Cl₂</td>
<td>81</td>
<td>19</td>
<td>900</td>
<td>320</td>
<td>0.9</td>
</tr>
<tr>
<td>HAA in CH₃Cl₂</td>
<td></td>
<td></td>
<td></td>
<td>323</td>
<td></td>
</tr>
<tr>
<td>C₆H₆</td>
<td>74</td>
<td>26</td>
<td>945</td>
<td>429</td>
<td>0.9</td>
</tr>
<tr>
<td>HAA in C₆H₆</td>
<td></td>
<td></td>
<td></td>
<td>431</td>
<td></td>
</tr>
</tbody>
</table>

In Table 4 some NMR measurements on acetylacetone solutions are recorded. HAA in the enol form is characterized by one HO-group for each $-\text{CH}_2$- group. As expected, the ratio HO-/$\equiv\text{CH}$ is about 1 in the non-polar solvents CCl₄ and C₆H₆. However, in CHCl₃ the ratio is only 0.5 (32°C), indicating a change in the surrounding of the enol group. The chemical shift from about 920 to about 820 cps indicates a weakening of the enol hydrogen bond. A chemical shift is also observed for the hydrogen in CHCl₃ when HAA is dissolved. The conclusion must be drawn that CHCl₃ and HAA interact with each other over the hydrogen in CHCl₃ and in the neighbourhood of the enol-group in HAA. Probably the intramolecular hydrogen bond of the enolic form is changed by the formation of a new hydrogen bond between the carbonyl group and the chloroform hydrogen.

Increasing the temperature leads to an increase in the HO-/$\equiv\text{CH}$ ratio, indicating a dissociation of the HAA—CHCl₃ bond. Since $k_d$ also decreases with temperature, it may be assumed that "unsolvated" HAA is less soluble in CHCl₃ than is "solvated" HAA.

The assumption that a dipole-dipole bond is formed between HAA and CHCl₃, as well as between HAA and CH₃Cl₂, is further supported by the fact that $k_d$ is temperature dependent in these systems only. Our investigation indicates that there is no effect of temperature on $k_d$ for benzene, and a $\Delta S$ value of about 3 e.u. can be estimated. This is about 6 e.u. higher than that for the CHCl₃ system ($\Delta S = -3$ e.u.), which indicates that a more ordered structure is formed in the CHCl₃ phase, and a less ordered structure in the C₆H₆ phase, when HAA is extracted into these solvents from aqueous solutions.

Acknowledgements. The economic support of the Swedish Atomic Research Council is gratefully acknowledged. We are also indebted to Drs J. O. Liljenzin and H. Reinhardt, and to Mrs. E. Norman for stimulating discussions and valuable experimental aid.

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Received February 18, 1969.