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99. Effect of an External Electric Field on the Decay Constant of $^{99}\text{Tc}^m$ in Halogen Complexes

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(22. II. 72)

Summary. A positive change $\Delta\lambda/\lambda$ of the decay constant of $^{99}\text{Tc}^m$ has been observed on the application of an external electric field in K_2TcX_6 (X = F, Cl, Br, I). For its investigation the Tc-complexes were embedded as small conglomerates or more or less as isolated single molecules in a powder of high dielectric constant, which was then compressed into a thin layer of about 0.2 mm and inserted between two capacitor plates. The change $\Delta\lambda/\lambda$ depends on the strength of the chemical bond of $^{99}\text{Tc}^m$. As a first approximation $\Delta\lambda/\lambda$ was assumed to be linearly dependent upon the electric field. The experimental results with an external field of 10^4 V/cm are:

Compound	K_2TcI_6	K_2TcBr_6	K_2TcCl_6	K_2TcF_6
$2 \times 10^5 \Delta\lambda/\lambda$	6.1 ± 0.9	5.2 ± 0.7	5.9 ± 0.8	2.2 ± 0.9

A relationship between $\Delta\lambda/\lambda$ and the electro-negativities of the ligand atoms could be established. Difficulties encountered in the theoretical calculation of $\Delta\lambda/\lambda$ are discussed.

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1. Introduction. – $^{99}\text{Tc}^m$ is one of the best investigated nuclides concerning half-life alterations. In 1953 *Bainbridge et al.* first detected distinct differences in the decay constant of $^{99}\text{Tc}^m$ in different chemical environments [1]. Subsequently other authors describe the influence of pressure, temperature and superconductivity on the half-life of $^{99}\text{Tc}^m$ [2]. The magnitude of the measured relative changes $|\Delta\lambda/\lambda|$ was in the range of 10^{-5} to 10^{-3} . The high sensitivity of $^{99}\text{Tc}^m$ to factors producing half-life alterations is a direct consequence of its unique decay scheme (Fig. 1).

The γ -transition *E3*, with a decay energy of 2.15 keV, is almost completely converted. For energetic reasons only the electrons of the M, N, and O shells can take part in internal conversion, i.e. the decay probability depends on the electron density of these outer electrons only. Therefore it is much easier to influence the decay time in the case of $^{99}\text{Tc}^m$, than for nuclides where the inner electrons contribute predominantly to the conversion.

In this work the influence of an external electric field on the decay constant of $^{99}\text{Tc}^m$ in K_2TcX_8 ($\text{X} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) is investigated.

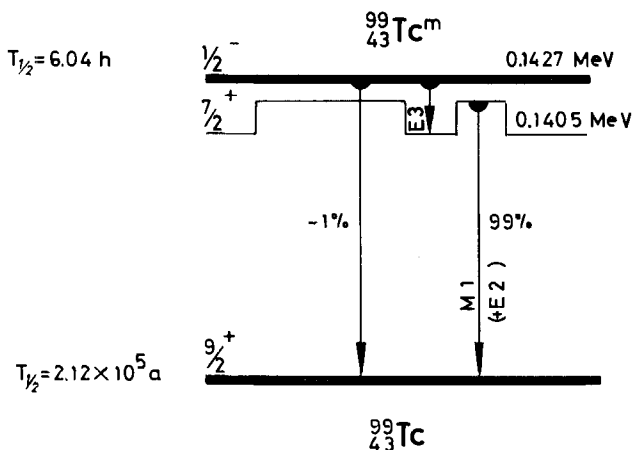


Fig. 1. Decay scheme for $^{99}\text{Tc}^m$ [3] [4]

2. Principle of measurement. – To determine half-life alterations with precision, the principle of relative measurement must be used. Thus the decay rates are observed for two practically identical radioactive sources differing only by the presence of an electric field applied to one of them. The apparatus to measure the resultant half-life alterations contains an automatic sample changer and a programmed registration of the decay rates. This technique has been previously described in detail [5] [6]. Both the step method (*Sprungmethode*) and the slope method (*Steigungsmethode*) were used [6] to determine the relative change of the decay constant $\Delta\lambda/\lambda$. In the step method the electric field is applied alternately to each of the sources, with the field at the other source kept at zero. In case of a non-zero $\lambda\lambda/\lambda$ the ratio F of the activities of the sources undergoes the following change $\Delta F/F$ as their electric field conditions are interchanged:

$$\frac{\Delta F}{F} \approx 2 \frac{\Delta\lambda}{\lambda}. \quad (1)$$

The slope method consists in measuring the ratio $F(t)$ over a period of about two half-lives keeping the electric field strength at one of the sources constant. As a first approximation $F(t)$ can be computed as follows:

$$F(t) \approx \frac{\Delta\lambda + \lambda}{\lambda} c (1 - \Delta\lambda t). \quad (2)$$

To decrease the influence of background and dead-time, $F(t=0)$ is chosen to be ≈ 1.000 . Thus the constant c is ≈ 1.000 .

3. Production of high electric fields. - To obtain an intensive electric field the Tc-compound was homogeneously mixed with a fine powder of a ceramic of high dielectric constant ($\epsilon \approx 6000$), which was then inserted between two capacitor plates (Fig. 2).

If the Tc-compound is monomolecularly distributed, the local electric field strength E_1 at the site of the Tc-compound can be estimated [7]:

$$E_1 \approx \frac{\bar{\epsilon} + 2}{3} E_{\text{ext}}. \quad (3)$$

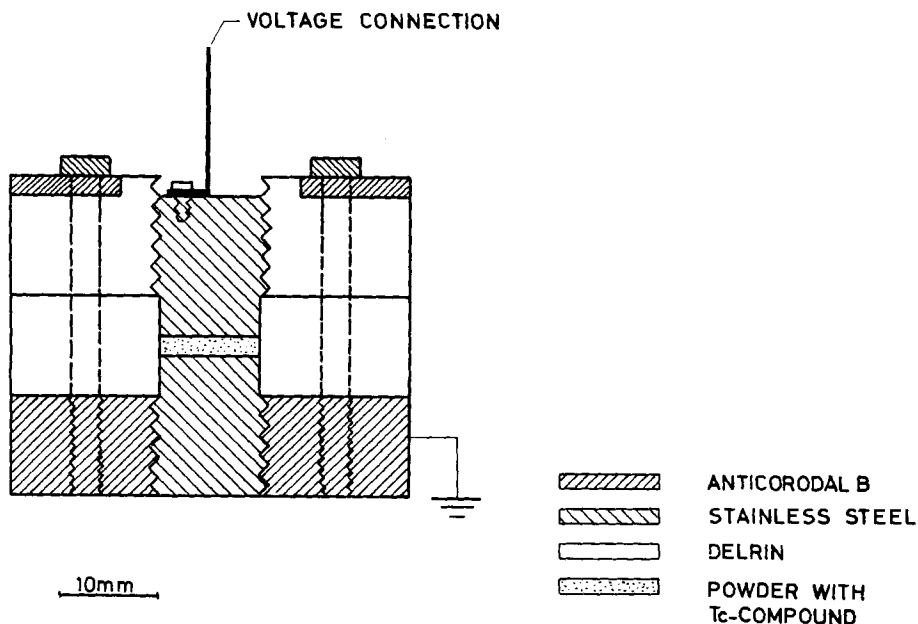


Fig. 2. Capacitor which serves as sample holder

E_{ext} is the external electric field strength and $\bar{\epsilon}$ the average dielectric constant of the powder - Tc-compound mixture.

On the other hand, if the Tc-compound is nonhomogeneously distributed in agglomerations of different size, we have the following field strength E_2 at the site of the Tc-compound [8]:

$$E_2 \approx \frac{3\bar{\epsilon}}{2\bar{\epsilon} + 1} E_{\text{ext}}. \quad (4)$$

For $\bar{\epsilon} \gg 1$ E_2 is $1.5 E_{\text{ext}}$. A typical value of $\bar{\epsilon}$ is 300. To avoid depolarisation effects in the capacitor, a 50 cycle a.c. voltage of constant peak amplitude was used for the production of the electric field.

4. Sample preparation. - Two different methods of sample preparation were used; of these the first, I, was chosen for better fulfilment of the assumptions involved in equation (3). For practical reasons, in preliminary experiments, NaTcO_4 -sources were made available. For this purpose a fine dielectric powder was added directly to ca. 3 mCi of carrier-free $^{99}\text{Tc}^m$ in the form of NaTcO_4 dissolved in 2-butanone and the solvent was subsequently evaporated. The powder with the adsorbed NaTcO_4 was then dried and poured into the capacitor, where it was compressed to a thin layer of thickness 0.15 mm to 0.2 mm (Fig. 2). Na_2TcCl_6 sources required, in addition, pre-treatment by the addition of 1 ml ethanol and two drops of conc. HCl to the solution in 2-butanone containing the $^{99}\text{Tc}^m$. It was very difficult to produce samples of uniform quality by this method, only every twentieth was successful, probably due to the presence of impurities. Samples prepared by method I have the advantage of a relatively large local electric field E_1 , at the site of the Tc-compound. However, the required small volumes of the Tc-compound make its chemical structure uncertain. Therefore a second, preparative method, II, which gives in principle exactly the desired compound, but at the cost of a smaller local electric field, was subsequently used. First, the compounds K_2TcX_6 ($X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) were prepared as described by Schwöschau [9]. The compounds were then labelled with the isomeric $^{99}\text{Tc}^m$ by recrystallisation of K_2TcX_6 in the presence of $^{99}\text{Tc}^m$. Usually 0.5–1.0 mg of the dried, labelled compound was added to 50 mg of dielectric powder and thoroughly mixed by grinding in a mortar. With this preparative method the local electric field E at the site of the Tc-compound is expected to be $E_1 > E > E_2$ [compare equation (3) and (4)].

5. Experimental results. - The relatively high electric field strength, obtained with source preparative method I, at the site of the Tc-compound induces an easily observable change of the decay constant (Fig. 3 and Fig. 4). Fig. 3 shows the measurement of $2 \Delta\lambda/\lambda$ by the step method. Fig. 4 demonstrates the slope method (twice) as well as the step method. The results obtained in this experiment are in good agreement with each other [10].

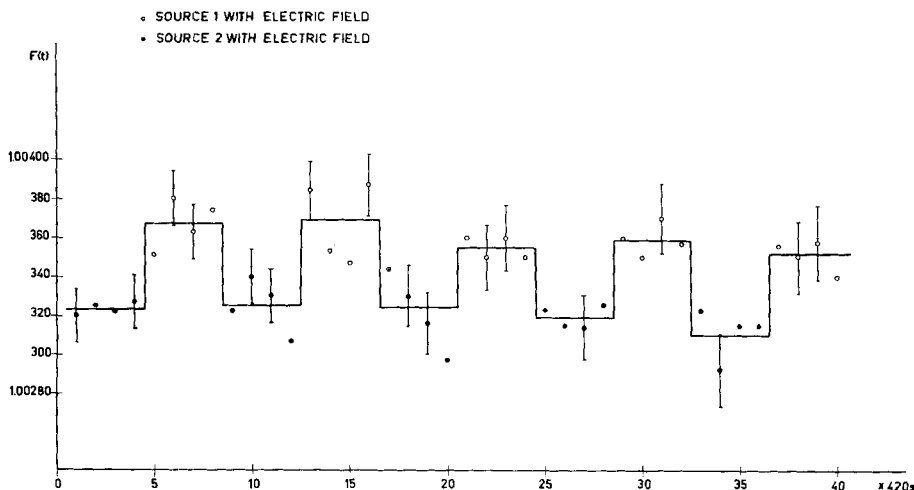


Fig. 3. The step method: The value for $2 \Delta\lambda/\lambda$ is $(40 \pm 4) \times 10^{-5}$ at an external electric field strength of 1.2×10^4 V/cm. The NaTcO_4 source was prepared by method I.

For chemical reasons the actual sources had to be prepared by method II (see sample preparation). Due to the obviously smaller local electric field strength at the site of

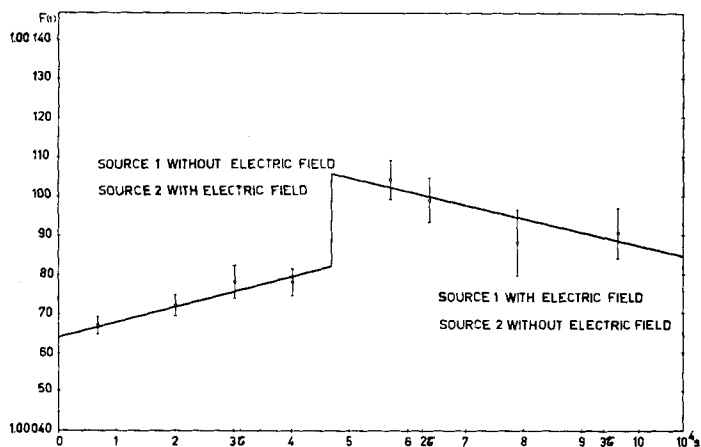


Fig. 4. Two measurements of $\Delta\lambda/\lambda$ by the slope method ($\Delta\lambda/\lambda = (12 \pm 2) \times 10^{-5}$ and $(11 \pm 4) \times 10^{-5}$ respectively). After 4.7×10^4 s the electric fields at the sources were interchanged, the resulting step in $F(t)$ was $2 \Delta\lambda/\lambda = (24 \pm 4) \times 10^{-5}$ (step method). The external electric field strength was 2×10^4 V/cm. The source, $\text{Na}_2^{99}\text{Tc}^m\text{Cl}_6$, was prepared by method I. [$\tau = 1/\lambda$, compare equation (2)].

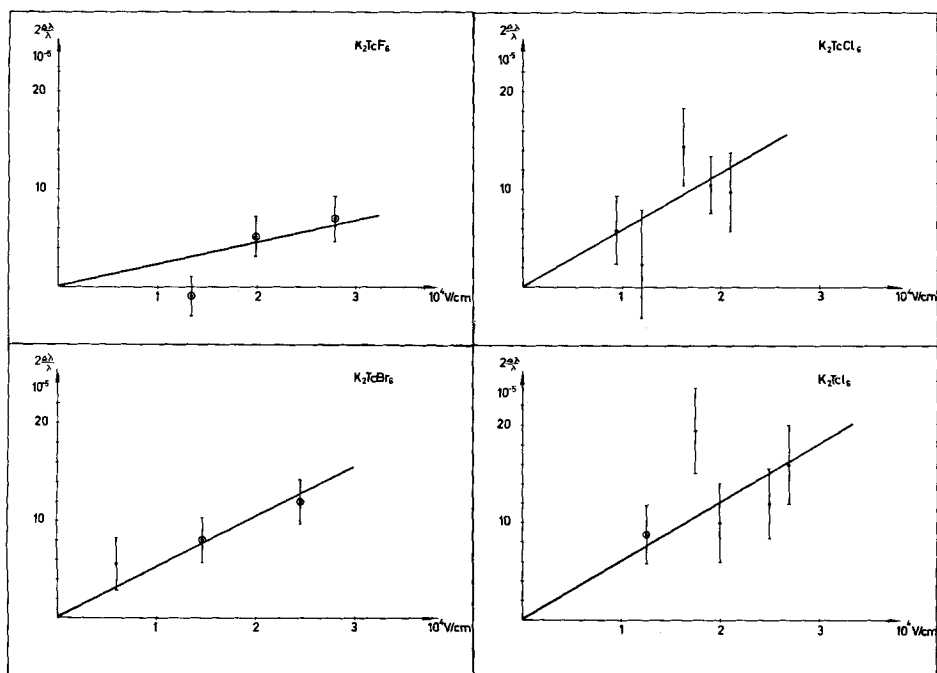


Fig. 5. Results of $2 \Delta\lambda/\lambda$ at different external electric field strengths for the Tc-halogen complexes. The results marked \odot are averages of two measurements.

the Tc-compound, these sources showed a smaller change of the decay constant. The step method was used in this case as it is less sensitive to electronic drift of the apparatus [6]. In Fig. 5 the dependence of $2\Delta\lambda/\lambda$ upon the external electric field strength is shown for K_2TcX_6 ($X = F, Cl, Br, I$).

Unfortunately the results obtained are not significant enough to establish a linear dependence. However, for comparison, the electric field dependence was approximated in each case by a straight line constrained to pass through zero. The lines shown in Fig. 5 were obtained by a least square fit. The resulting average $2\Delta\lambda/\lambda$ values for the different chemical compounds are compared for a common external electric field strength of $1 \times 10^4 V/cm$ in Table 1. The errors shown are statistical only. Possible systematic errors originating from the experimental method were discussed in detail earlier [6] [11] but are not included in this error analysis.

Table 1. Values of $\Delta\lambda/\lambda$ for different Tc-complexes at a normalized field strength of $E_{ext} = 1 \times 10^4 V/cm$.

Compound	K_2TcI_6	K_2TcBr_6	K_2TcCl_6	K_2TcF_6
$2 \times 10^5 \Delta\lambda/\lambda$	6.1 ± 0.9	5.2 ± 0.7	5.9 ± 0.8	2.2 ± 0.9

6. Discussion. - a) *Electric field induced half-life alteration and chemical parameters.* The experimental results show that the $^{99}Tc^m$ nuclide in the halogen complexes decays faster in the presence of an external electric field. Fig. 6 shows the normalized $\Delta\lambda/\lambda$ values of Table 1 plotted vs. the electro-negativities of the ligand atoms. The $KTcO_4$

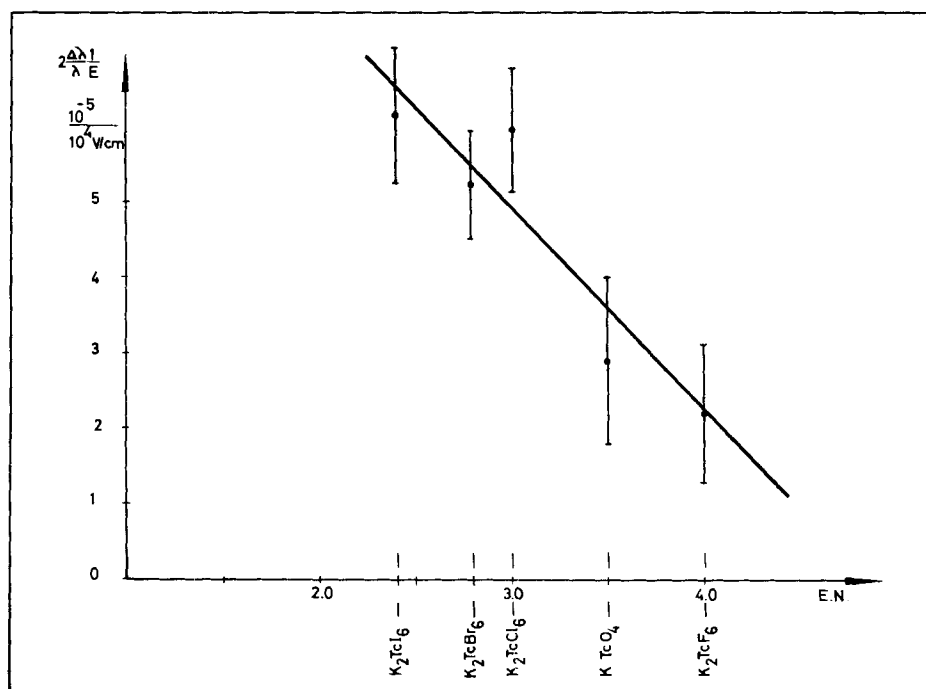


Fig. 6. Normalized $\Delta\lambda/\lambda$ values of Table 1 plotted vs. the electro-negativities of the ligand atoms.

result previously obtained [11] is included in this diagram for comparison. Similar not inconsistent [12] correlations can be obtained as a function of the ligand field parameter $10 Dq$ [9] or of the valence force constants [13]. All of these parameters more or less describe the strength of the chemical bonding. As Table 1 and Fig. 6 show, it seems reasonable that the bonding of the more stable and less voluminous complexes are less influenced by an electric field.

b) *Theoretical considerations.* Due to the complicated bonding character of the investigated complexes only a qualitative interpretation of the results was attempted. Fig. 7 shows the molecular orbitals of the undistorted octahedral halogen complexes. The effect of an external electric field can be interpreted as a change in the electron population of the binding and antibinding molecular orbitals. This causes a change of the electron density $\Delta |\psi(0)|^2 / |\psi(0)|^2$ near the Tc-nucleus. In the case of $^{99}\text{Tc}^m$, only electrons of the M, N, and O shells need to be considered as mentioned previously. According to Slater [14] and Perlman [15], mainly the $4p_{1/2}$, $4p_{3/2}$ and to a lesser extent the $4d_{3/2}$ electrons contribute to the internal conversion. For a conversion coefficient $\alpha \gg 1$, the relative change of the decay constant $\Delta\lambda/\lambda$ equals $\Delta\alpha/\alpha \approx \Delta |\psi(0)|^2 / |\psi(0)|^2$ [16]. Table 2 shows the change of the electron density near the nucleus when the binding character of the valence electrons is altered.

When estimating half-life alterations it is possible that only orbitals responsible for the electron charge transfer spectrum or those taking part in the ligand field transitions need to be considered. A first estimate of a half-life alteration has been

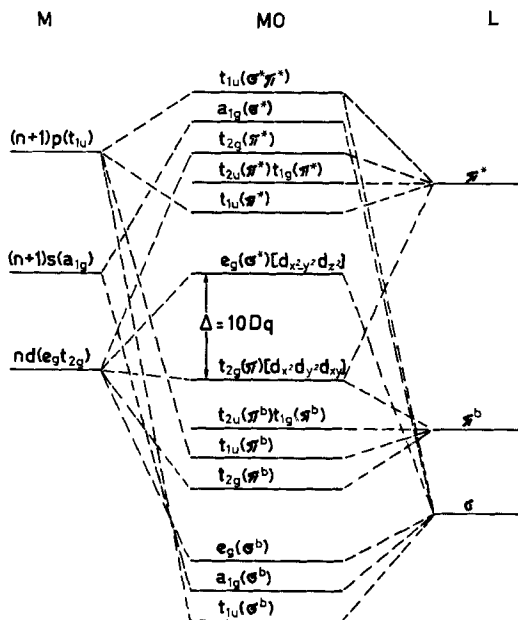


Fig. 7. Molecular Orbital (MO) energy level diagram for octahedral transition metal halogen complexes [17] [18]

M = Metal Orbitals, L = Ligand Orbitals, $\Delta = 10 Dq$ = Ligand Field Parameter.

Table 2. Change of the electron density $\Delta|\psi(0)|^2$ near the nucleus of the central ion in octahedral 4d-transition metal complexes as a function of electron transfer processes [17].

Electron transfer			$\Delta \psi(0) ^2$
1.	σ_L	$\rightarrow \sigma_M(4d)$	<0
2.	π_L	$\rightarrow \pi_M(4d)$	<0
3.	$\pi_M(4d)$	$\rightarrow \pi_L$	>0
4.	σ_L	$\rightarrow \sigma_M(5s)$	>0
5.	σ_L, π_L	$\rightarrow \sigma_M(5p), \pi_M(5p)$	<0

made [11] by approximating $\Delta|\psi(0)|^2/|\psi(0)|^2$ to the relative change of the valence electron density within a diatomic molecule to which an electric field is applied. For this purpose the perturbation calculation of *Bloembergen & Dixon* [19] was used, omitting *Sternheimer* shielding effects. Two different theoretical estimates were obtained with the same theoretical approach but with different chemical parameters (Table 3).

Table 3. Theoretically estimated values of $\Delta\lambda/\lambda \times 1/E$ assuming a linear electric field dependence. The two columns represent different estimates of $\Delta\lambda/\lambda \times 1/E$, using different chemical parameters such as the electronic polarizability β of the ligand atom [*Pauling* value] or the interatomic distance R [13]. A common ligand field parameter A is used in both cases [9].

K_2TcX_6	$\frac{\Delta\lambda}{\lambda} \times \frac{1}{E} (\beta, A) \left[\frac{10^{-6}}{10^4 \text{ V/cm}} \right]$	$\frac{\Delta\lambda}{\lambda} \times \frac{1}{E} (R, A) \left[\frac{10^{-6}}{10^4 \text{ V/cm}} \right]$
X = F	0.57	4.0
= Cl	1.16	5.4
= Br	1.30	5.9
= I	1.72	7.0

Both results yielded the right order of magnitude of the observed effects and, at first approximation, also the dependence on the different halogen ligands. This is somewhat surprising, and perhaps fortuitous, since the exact (inhomogeneous) field distribution at the site of the Tc-complexes is not known and since, in addition, we are dealing with a polyatomic structure for which the required molecular symmetry C_{4v} (distorted octahedral arrangement) [11], although not inconsistent with some previous experimental work [23], may not be fulfilled. However, the experimental set-up with the heterogeneous dielectric cannot exclude *a priori* the discussed linear electric field effect.

Mössbauer isomer shift spectroscopy is a useful tool for investigating chemical bonding [20]. *K. Alder et al.* [21] mention that the determination of half-life alterations, combined with the measurement of *Mössbauer* chemical shifts, yield sufficient information to settle the calibration problem [17] of the *Mössbauer* chemical shifts. *Drickamer* [22] uses high pressure experiments in order to keep constant as many chemical parameters as possible. An alternative approach would be to effect corresponding experiments with an exactly known electric field applied to the molecules under investigation, or – to expand the field idea – the application of electro-magnetic

fields in the optical region to induce different electron populations by electron charge transfer within the molecules.

We regret extremely the sudden and too early death of Prof. *P. Huber*, initiator of $\Delta\lambda/\lambda$ experiments in Basle. We thank Prof. *K. Alder* for many helpful comments and discussions and Prof. *H. R. Striebel* for his advice and criticism of the manuscript. We acknowledge the work done by *F. Abt* (electronic workshop) and by *H. Weyeneth* (mechanical workshop). This research was made possible through the financial support of the *Swiss National Foundation*.

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100. Addition von Phthalidnatrium an 2-Carbäthoxy-8-methoxy-naphthochinon; eine neue Synthese für Hydroxy-naphthacenchinone

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(7. 1. 72)

Summary. A simple method to synthesize hydroxysubstituted naphthacenequinones is described. Phthalide anion adds to negatively substituted quinones, e.g. ethyl-8-methoxy-naphthacenequinone-2-carboxylate. Acid catalysed cyclisation of this adduct under simultaneous decarboxylation yields a substituted naphthacene quinone.

¹⁾ Aus der Dissertation von *Werner Trueb* [1]; jetzige Adresse: *Sandoz AG*, Basel.