The Study of Reduction Mechanism of *N,N'*-Disubstituted Amidines by Means of Kalousek Commutator

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A transistor Kalousek commutator was designed. For its construction, a polarized relay with a very short switching time was used as the proper switching element. This relay was excited by a transistor circuit and fed by a build-in battery. The commutator thus constructed allows a continuous change of switching frequency over a wide range (0—45 Hz).

By means of this commutator, the character of the electrode process for the electroreduction of *N,N'*-diphenylbenzamidine was investigated. It was found that the first reduction wave corresponded to an irreversible electrode process, whereas the second one was due to a reversible process. On the basis of this statement, a reduction mechanism for *N,N'*-disubstituted amidines was proposed.

For a complex electrochemical study of some types of amidines [1], the character of their electrode reactions had to be examined. The method of Kalousek commutator was chosen for this purpose. Since the earlier constructions of commutators [2—5] had been based on the use of obsolete technical means and no commercial commutator was available, a new transistor Kalousek commutator was designed.

Experimental

The construction of commutator

The main element of commutator remains a polarized relay. It is due to the fact that it is necessary to avoid any supply of parasitic signals regarding the rather small signals (10^{-6} A) in the proper measuring circuit of polarograph because it would bring about a direct galvanic connection of the switched electric circuit.

The switching frequency of the polarized relay is controlled by a transistor multivibrator in a usual connection. The adjustment of multivibrator frequency is carried out by a simultaneous change of resistances in the feeding circuits of the base of both transistors. A simultaneous change of resistances is necessary in order that the duty ratio 1 : 1 should be held. In this manner, a change of the time constant of both R—C circuits or a change of frequency is achieved. To prevent inadmissible changes of the parameters of free working point of both transistors the whole range 0—45 Hz is divided in four partial ranges. The change of range is performed by switching fixed condensers (Fig. 1).

The instrument is fed by a battery (9 V) and built in a standard metallic box Tesla.

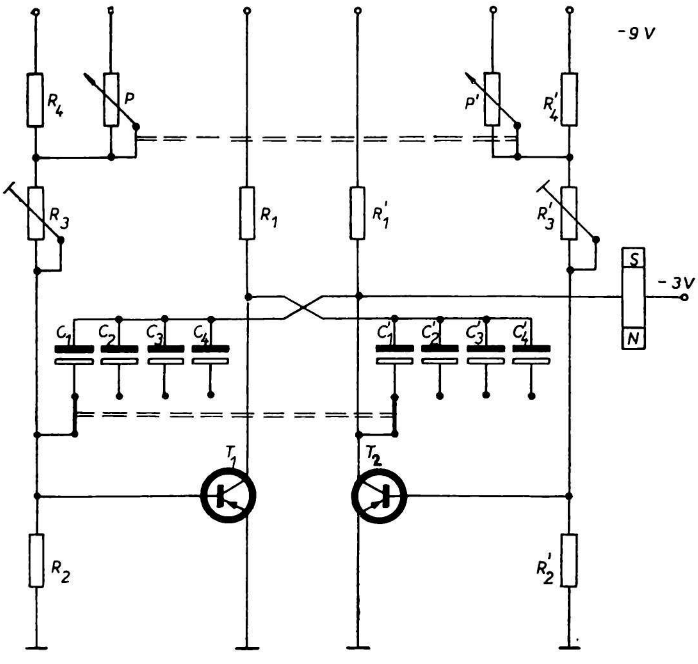


Fig. 1. Circuit diagram of Kalousek commutator.
T_1, T_2 transistors OC 72; R_1, R_1' resistances TR 101, 10%, 820; R_2, R_2' resistances TR 107, 20%, 2k2; R_3 potentiometer trimmer WN 790, 30, 3k2; R_3' potentiometer trimmer WN 790, 30, 2k2; R_4 R_4' resistances TR 101, 10%, 12k; P, P' potentiometers 25 k/N; C_1, C_1' condensers TC 924, 2M; C_2, C_2' condensers TC 922, 5M; C_3, C_3' condensers TC 923, 10M; C_4, C_4' condensers TC 922, 20M; polarized relay HL 100, Tesla.

The study of electrode process character for the electroreduction of N,N'-diphenylbenzamidine

By means of the commutator described, the character of the electroreduction of *N,N'*-diphenylbenzamidine, prepared according to *Gerhardt* [6], was investigated. The purity of preparation was checked by melting point (150°C) and nitrogen content determination.

Earlier polarographic studies of *N,N'*-disubstituted amidines [1, 7] demonstrated that the reduction of this group took place in two two-electron waves of an explicit diffusion character. The more positive of both waves, which can be seen in the range of pH 4—12, decreases in a form of dissociation curve of weak electrolyte. At about pH 5, another wave appears the height of which increases with increasing pH first, but at higher pH (about 9) a decrease of limiting current is evident.

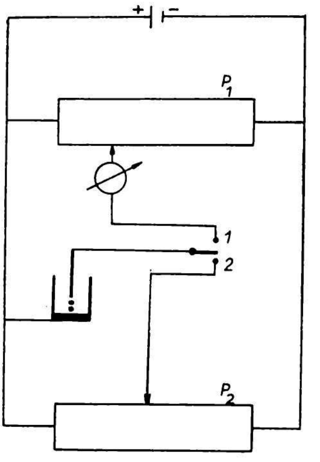
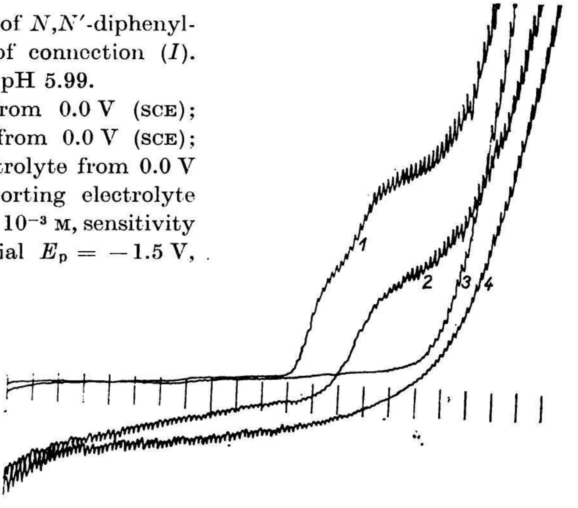


Fig. 2. Block diagram of Kalousek commutator. P_1 potentiometric drum of polarograph; P_2 auxiliary potentiometer.

For the study of reversibility, two circuits (*I* and *II*) were applied. In the first circuit (*I*) [8], the galvanometer is connected to the sliding contact of potentiometric drum of the polarograph and the dropping mercury electrode, *i.e.* between point *1* and polarographic bridge P_1 (Fig. 2). In this case, the current flows through the galvanometer only during polarization of the dropping mercury electrode by the voltage drawn from the polarograph. After commutating, the dropping mercury electrode is polarized by a constant voltage from the auxiliary potentiometer P_2 and current does not flow through

Fig. 3. Normal and switched curve of *N,N'*-diphenylbenzamidine obtained by means of connection (*I*). Britton—Robinson buffer pH 5.99.
1. normal curve of depolarizer from 0.0 V (SCE); *2.* switched curve of depolarizer from 0.0 V (SCE); *3.* normal curve of supporting electrolyte from 0.0 V (SCE); *4.* switched curve of supporting electrolyte from 0.0 V (SCE); 100 mV/absc., $c = 10^{-3}$ M, sensitivity 1 : 300, constant auxiliary potential $E_p = -1.5$ V, $f = 6$ Hz.



the galvanometer. In the second circuit (*II*) the galvanometer is connected in an arm of the auxiliary potentiometer P_2, *i.e.* between point *2* and auxiliary potentiometer P_2

(Fig. 2). In this case the current flows through the galvanometer only during polarization of the dropping mercury electrode by the constant voltage from the auxiliary potentiometer.

In both cases the polarograph LP 55 was used as an auxiliary potentiometer while the instrument LP 60 with a recorder EZ 2 was used as a proper polarograph. The sensitivity of recorder was chosen 5×10^{-7} A for the whole scale.

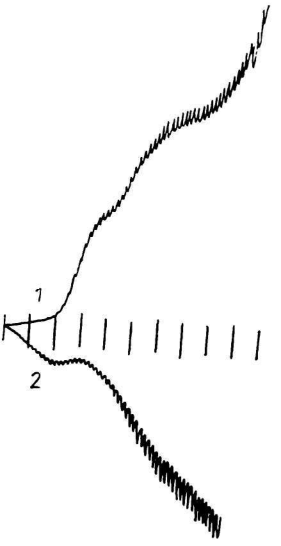


Fig. 4. Normal and switched curve of N,N'-diphenylbenzamidine obtained by means of connection (*II*). Britton—Robinson buffer pH 5.99. *1.* normal curve of depolarizer from −0.9 V (SCE); *2.* switched curve of depolarizer from −0.9 V (SCE); 100 mV/absc., $c = 10^{-3}$ M, sensitivity 1 : 300, constant auxiliary potential $E_p = -0.9$ V, $f = 12$ Hz.

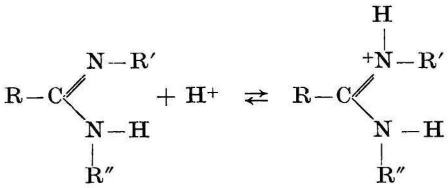
For the study of polarographic curves by means of Kalousek commutator, a 10^{-3} M solution of N,N'-diphenylbenzamidine in ethanol was prepared. Before recording the curves, 2 ml of this solution a 2 ml of Britton—Robinson buffer were mixed. After removing the oxygen by nitrogen, the record was performed by using Kalousek vessel with a saturated calomel electrode and a dropping mercury electrode with constants $t_1 = 2.8$ sec, $h = 30$ cm. After this record, the solutions were removed and their pH measured by means of Beckman pH-meter, model G.

Normal and commutated curves of N,N'-diphenylbenzamidine are presented in Fig. 3 for circuit (*I*) and in Fig. 4 for circuit (*II*).

The results obtained make possible to draw conclusion that the first reduction wave of N,N'-diphenylbenzamidine corresponds to an irreversible electroreduction while the second one is due to a reversible electroreduction.

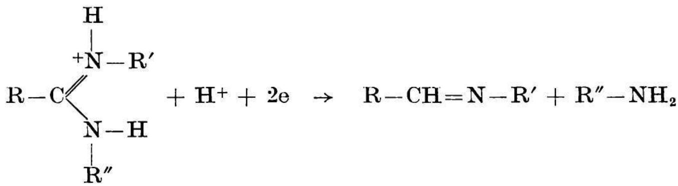
Discussion

Since it has been proved by polarographic electroreduction of disubstituted amidines [1, 7] that the reducible form is a cation, arising according to (*A*):



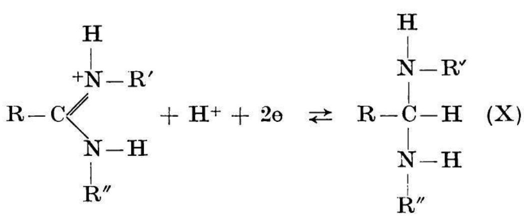
(A)

it can be assumed that the reduction of this group of substances may run in two principal ways (*B*—*E*). In both cases *N*-benzylaniline is the final product which can be formed either by reduction of benzalaniline, arising as an intermediate product according to equations (*B*) and (*C*), or by reduction of an instable intermediate product X, according to equations (*D*) and (*E*):

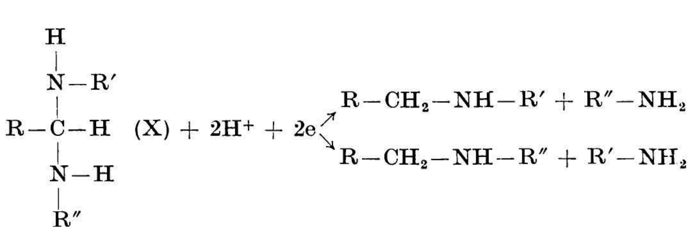


(B)

$$R-CH=N-R' + 2H^+ + 2e \rightleftarrows R-CH_2-NH-R' \qquad (C)$$



(D)



(E)

Since the second wave has been found reversible, the reduction according to (*D*) and (*E*) can be excluded because this reduction scheme supposes the reversibility of the first wave. This fact is not conform with the present knowledge of the reduction mechanism of amidines [7] which has been deduced by analogy from the reduction mechanisms of amidoximes.

The view that the reduction runs according to (*B*) and (*C*) is supported by the fact that the reduction of benzalaniline is reversible [9]. It has also been found that the half-wave potentials of the second waves of *N*,*N*′-diphenylbenzamidine and benzalaniline are identical and practically independent on pH. In the case of electroreduction on a large surface electrode in the range of pH where *N*,*N*′-diphenylbenzamidine gives only a single wave (pH about 4.4), the benzalaniline has been identified as a reaction product [9]. Higher values of pH having been applied, the electroreduction of both *N*,*N*′-diphenylbenzamidine and benzalaniline causes the formation of the same *N*-benzylaniline, which can be isolated.

In the basis of the measurements performed, the conclusion may be drawn that the polarographic reduction of *N*,*N*′-disubstituted amidines probably runs according to the mechanisms expressed by equations (*B*) and (*C*).

References

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