

## On the Electrochemical Oxidation of Enamines

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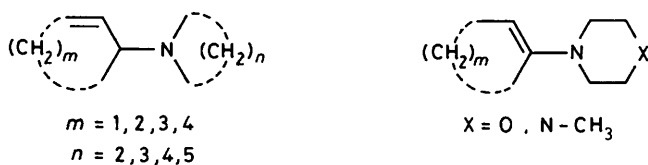
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The electrochemical oxidation properties of enamines of the cyclic ketones cyclo-pentanone, -hexanone, -heptanone, and -octanone with the cyclic amines pyrrolidine, piperidine, 1-methylpiperazine (1-MP), morpholine (MO), hexa-, and hepta-methyleneimine are investigated with the aid of cyclic voltammetry. The oxidations are totally irreversible. The lifetime of the intermediate cation radicals are shorter than 0.2 ms as determined by double potential step chronoamperometry. The anodic peak potentials depend on the amine component in the order of ring sizes  $5 < 7; 8 < 6 < 1\text{-MP} < \text{MO}$ . The variation of the ketone component shows no significant influence on the peak potentials. The ionization potentials of the enamines were measured and correlated with the anodic peak potentials.

Since Stork *et al.*<sup>1,2</sup> utilized enamines as reactive intermediates for the alkylation and acylation of carbonyl compounds, their synthetic utility has grown rapidly as documented in a variety of pertinent reviews<sup>3</sup> and monographs.<sup>4</sup> Of great interest are the factors which determine structure and reactivity of enamines. Hitherto, they have been characterized with spectroscopic methods, such as <sup>1</sup>H, <sup>13</sup>C, and <sup>15</sup>N n.m.r. and photoelectron spectroscopy.<sup>5</sup> Also X-ray structure analyses<sup>6</sup> as well as quantum chemical investigations<sup>7</sup> have been reported.

Only a few investigations have been concerned with the electrochemistry of enamines. Shono *et al.*<sup>8</sup> and Chiba *et al.*<sup>9</sup> have utilized electrochemical oxidation for synthetic purposes. In addition Huang and Hsu<sup>10</sup> studied the oxidation of *cis*-1-(4-morpholino)-1,2-diphenylethene while Fritsch *et al.*<sup>11a</sup> investigated the electrochemical properties of alkenes substituted with dimethylamino groups. For a few cases the reduction properties of some enamines have been reported.<sup>11b</sup>

In the present work the electrochemical oxidation properties of all enamines constituted of the cyclic ketones cyclo-pentanone, -hexanone, -heptanone, and -octanone with the cyclic amines pyrrolidine, piperidine, 1-methylpiperazine, morpholine, hexa-, and hepta-methyleneimine have been systematically investigated. In detail we report on the



following aspects: (1) irreversibility of the oxidation process; (2) lifetimes of the intermediate cation radicals; (3) the anodic peak potentials compared with the corresponding ionization potentials of the enamines.

### Results and Discussion

(1) *Irreversibility in the Oxidation Process.*—A typical cyclic voltammogram of an enamine, 1-(cyclo-oct-1-en-yl)piperidine, is shown in Figure 1. The voltammograms of all investigated enamines show well defined anodic current maxima, but no corresponding cathodic wave on the reverse scan, even at rates up to  $1000 \text{ V s}^{-1}$ . In addition we have tested the effect of temperature. Even at  $-100^\circ\text{C}$  (in butyronitrile-0.1M-Bu<sub>4</sub>NBF<sub>4</sub>) the oxidation process remains irreversible, *i.e.* a cathodic wave does not show up.

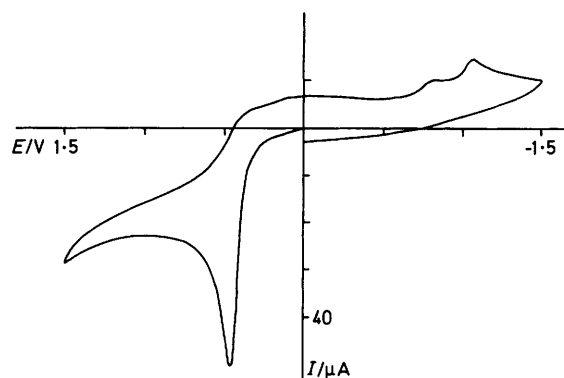
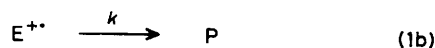
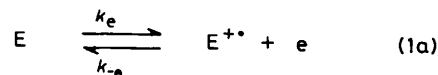


Figure 1. Cyclic voltammogram of  $1.63 \times 10^{-3} \text{ M}$ -1-(cyclo-oct-1-en-yl)-piperidine in acetonitrile-0.1M-Bu<sub>4</sub>NBF<sub>4</sub>, sweep rate  $\nu$   $100 \text{ mV s}^{-1}$ , at a gold disk electrode



Scheme.

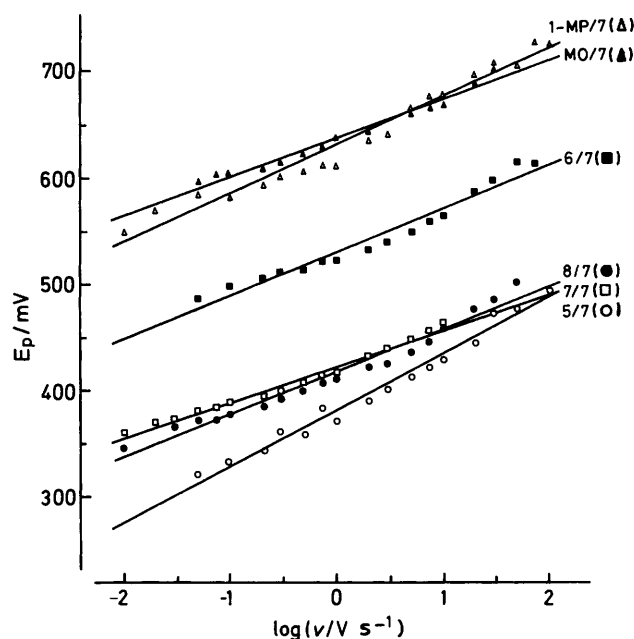
The oxidation process can be summarized by the Scheme. From the enamine E one electron is transferred to the electrode surface. The rate constant for this heterogenous electron transfer is  $k_e$ . The cation radical produced is very unstable; its lifetime is 0.2 ms (see Experimental section). The subsequent rate process (with rate constant  $k$ ) is much faster than the reverse electron transfer (rate constant  $k_{-e}$ ). Previous investigators<sup>8</sup> have shown that  $E^{+\bullet}$  reacts with the solvent. Electro-oxidation of enamines in methanol yields methoxyenamines. Hence we were not interested in further product analyses.

To establish the irreversible nature of the enamine oxidation process quantitative criteria were employed.<sup>12</sup>

(a) *Peak potentials.* According to Nicholson and Shain<sup>13</sup> for the process in the Scheme the relationship (2) holds where

$$E_p = \frac{2.303RT}{2\alpha nF} \log \nu + \text{const.} \quad (2)$$

$E_p$  is the peak potential,  $\alpha$  the transfer coefficient for the



**Figure 2.** Anodic peak potentials  $E_p$ /mV of the enamines derived from cycloheptanone versus  $\log(v/V s^{-1})$ . The concentrations in acetonitrile-0.1M-Bu<sub>4</sub>NBF<sub>4</sub> are:  $1.16 \times 10^{-3}M$ -5/7 (○),  $1.23 \times 10^{-3}M$ -6/7 (■),  $1.23 \times 10^{-3}M$ -MO/7 (▲),  $1.15 \times 10^{-3}M$ -1-MP/7 (△),  $1.36 \times 10^{-3}M$ -7/7 (□),  $1.45 \times 10^{-3}M$ -8/7 (●)

heterogeneous electron transfer, and  $n$  the number of electrons transferred in the rate-limiting step. Slopes  $> 30$  mV per decade are predicted for totally irreversible waves.

For convenience, we introduce a short-hand notation for the various enamines. In A/K A characterizes the ring size of the amine, while K refers to the ring size of the ketone; morpholine is abbreviated as MO, 1-methylpiperazine as 1-MP. In this notation, e.g. 5/7 means 1-(cyclohept-1-enyl)pyrrolidine, MO/7 is the corresponding morpholinoenamine.

An experimental verification of equation (2) is reported in Figure 2. It illustrates the dependence of the anodic peak potentials on the logarithms of the sweep rates. As representative examples the group of enamines derived from cycloheptanone are chosen. All slopes of the plots are  $> 30$  mV [the correlation coefficients for the linear regressions are  $r^2$  0.96–0.99]: 54 (5/7); 41 (6/7); 45 (1-MP/7); 36 (MO/7); 34 (7/7); 40 mV (8/7)]. These results provide evidence for a totally irreversible electron-transfer process. Similar trends are observed for the half-peak potentials  $E_{p/2}$  (here not recorded).

Figure 2 illustrates the dependence of the peak potentials on the structure of the enamines, e.g. the peak potential of the pyrrolidinoenamine 5/7 is the lowest, followed by 7/7 and 8/7. To complete these investigations the anodic peak potentials of all enamines were recorded at a sweep rate of  $v$  100 mV s<sup>-1</sup>. The results are listed in Table 1.

The peak potentials of the enamines depend on the ring size of the amine component in the order  $5 < 7, 8 < 6 < 1-MP < MO$ . The morpholinoenamines are the most difficult to oxidize and their peak potentials are ca. 0.2 V more positive than those of the pyrrolidinoenamines. Variation of the ring size of the ketone component causes only small differences in the peak potentials. These differences are within the accuracy range of the measurements.

(b) *Determination of transfer coefficients.* The transfer coefficients for the oxidation process were determined by three independent methods: (A) from the slope of the plot  $E_p = f(\log v)$ , as given in equation (2). (B) According to Nicholson and

**Table 1.** Anodic peak potentials  $E_p$ /mV of the enamines,  $v$  0.1 V s<sup>-1</sup>. A refers to the amine component and K to the ketone component

K	A					
	5	6	1-MP	MO	7	8
5	366	443	550	561	392	392
6	361	469	561	574	385	391
7	332	499	583	605	389	378
8	363	472	558	589	400	409

$$E_p = \frac{2.303RT}{\alpha nF} \log I_p + \text{const.} \quad (3)$$

Shain<sup>13</sup> the peak potential  $E_p$  for the irreversible case is given by equation (3). Again, from the slopes of the plots  $E_p = f(\log I_p)$ , where  $I_p$  is the peak current,  $\alpha$  can be determined. (C) A third, independent method results from the description of the width of the wave ( $E_p - E_{p/2}$ ) for an irreversible system which depends on  $\alpha$  according to equation (4).<sup>13</sup>

$$E_p - E_{p/2} = 1.857 \frac{RT}{\alpha nF} \quad (4)$$

The transfer coefficients of all enamines were determined by these three methods. The values obtained by the three methods (for irreversible systems) are in excellent accord with each other, for all enamines (not recorded in detail here). This further establishes the total irreversibility of the electron-transfer mechanism.<sup>12</sup>

Average values of the transfer coefficients of each enamine, determined by methods A–C\* are summarized in Table 2.

(c) *Calculation of the cyclic voltammetry waves.* For a totally irreversible system it is possible to describe the current by an equation which is based only on Fick's laws of diffusion and the potential dependence of the rate constant of the electron transfer [equation (5)].  $k_s$  is the rate constant at the standard potential  $E^0$ .

$$k_e(E) = k_s \exp \left[ \frac{\alpha nF}{RT} (E - E^0) \right] \quad (5)$$

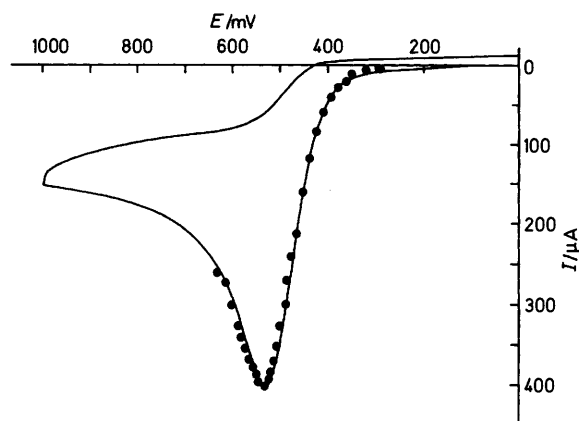
Nicholson and Shain<sup>13</sup> developed expression (6) for the current as a function of time.  $A$  is the area of the electrode,  $D$  is

$$I = nFAc(\pi Db)^{1/2} \chi(bt) \quad (6)$$

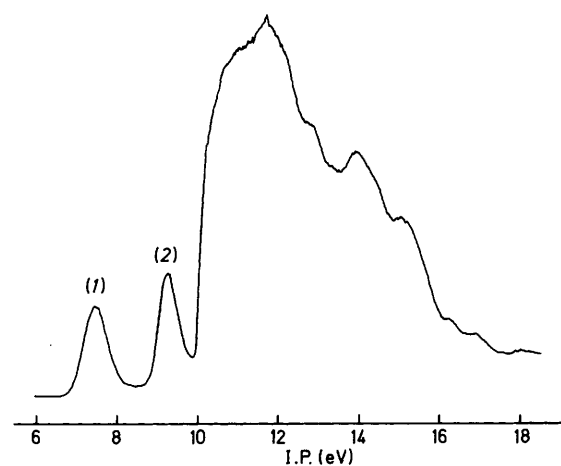
$$b = \frac{\alpha nFv}{RT}$$

the diffusion coefficient (see Experimental section). The function  $\chi(bt)$ , which Nicholson and Shain<sup>13</sup> have tabulated, comprises the potential dependence of the current. Since  $\alpha$  at a sweep rate  $v$  and the diffusion coefficient  $D$  which is determined by an independent method (see Experimental section) are known, the shape of the wave can be calculated according to expression (6). The agreement between theory and experiment is shown in Figure 3. It shows the experimentally determined cyclic voltammogram of the 6/8 enamine and the corresponding

\* It must be noted that the transfer coefficients  $\alpha$  determined by the width of the wave (method C) depend on the potentials  $E_p$ . With increasing peak potential  $E_p$  the waves become broader and the transfer coefficients  $\alpha$  decrease. In Tables 2 and 3 the average values of  $\alpha$  are presented. For a discussion of the potential dependence of the transfer coefficients see ref. 14.



**Figure 3.** Calculated and experimental cyclic voltammogram of the 6/8 enamine in acetonitrile-0.1M-Bu<sub>4</sub>NBF<sub>4</sub> at the scan rate  $v$  5 V s<sup>-1</sup>,  $\alpha$  0.68. The diffusion coefficient was  $D$  2.2.10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup> (see Experimental section). The calculated points are based on equation (6)



**Figure 4.** The He<sup>I</sup> photoelectron spectrum of 1-(cyclo-oct-1-enyl)piperidine

calculated wave. The latter was shifted along the potential axis to match the peak potential of the cyclic voltammogram. The measured peak is in almost perfect agreement with the calculated curve. Since relation (6) is only valid for an irreversible system the good agreement between theory and experiment confirms such a mechanism for electron transfer.

(2) *Correlation of Anodic Peak Potentials with Ionization Potentials.*—In addition to the electrochemical measurements we determined the photoelectron spectra (p.e.s.) of the enamines. A typical photoelectron spectrum of an enamine, 1-(cyclo-oct-1-enyl)piperidine, is recorded in Figure 4. The first two bands appear at (1) 7.48, and (2) 9.28 eV. They refer to ionization of electrons of the  $\pi$ -type allylic orbital system of the lone pair at the nitrogen atom with the adjacent double bond. The third band refers to a broad peak. Hence an unequivocal assignment of ionization potentials is only possible for the first two bands. A similar pattern is also observed for the other enamines. The first (vertical) ionization potentials,  $I_{p1}$ , thus obtained are listed in Table 3, together with the corresponding anodic peak potentials.

Regarding the  $I_p$  values the enamines derived from hexa- and heptamethyleneimine reveal the lowest and those from morpholine the highest values. On the other hand, in the electrochemical experiments the lowest peak potentials occur

**Table 2.** Average value by the three methods A—C of the transfer coefficients  $\alpha$  of each enamine. A refers to the amine component and K to the ketone component

		A					
		5	6	1-MP	MO	7	8
K	5	0.56	0.62	0.61	0.58	0.69	0.76
	6	0.87	0.64	0.82	0.84	0.79	0.81
	7	0.57	0.73	0.62	0.76	0.82	0.74
	8	0.64	0.67	0.72	0.80	0.89	0.79

**Table 3.** Anodic peak potentials  $E_p$ /mV,  $v$  100 mV s<sup>-1</sup>, in comparison with the first ionization potentials  $I_{p1}$ /eV

Enamine	$E_p$ /mV	$I_{p1}$ /eV
5/5	366	7.10 <sup>5m</sup>
6/5	443	7.40 <sup>5m</sup>
1-MP/5	550	7.39 <sup>a</sup>
MO/5	561	7.60 <sup>5m</sup>
7/5	392	6.96 <sup>a</sup>
8/5	392	6.92 <sup>a</sup>
5/6	361	7.10, <sup>5l</sup> 7.14, <sup>5m</sup> 7.15 <sup>5o</sup>
6/6	469	7.42, <sup>5l</sup> 7.50, <sup>5m</sup> 7.44, <sup>5n</sup> 7.54 <sup>5o</sup>
1-MP/6	561	7.53 <sup>a</sup>
MO/6	574	7.66, <sup>5l</sup> 7.67, <sup>5m</sup> 7.65 <sup>5n</sup>
7/6	385	7.00 <sup>a</sup>
8/6	391	6.97 <sup>a</sup>
5/7	332	7.25 <sup>a</sup>
6/7	499	7.53 <sup>a</sup>
1-MP/7	583	7.57 <sup>a</sup>
MO/7	605	7.68 <sup>a</sup>
7/7	389	7.16 <sup>a</sup>
8/7	378	7.14 <sup>a</sup>
5/8	363	7.06 <sup>a</sup>
6/8	472	7.47 <sup>a</sup>
1-MP/8	558	7.53 <sup>a</sup>
MO/8	589	7.72 <sup>a</sup>
7/8	400	6.94 <sup>a</sup>
8/8	409	6.96 <sup>a</sup>

<sup>a</sup> This work.

for the pyrrolidinoenamines. A plot of both quantities,  $I_{p1}$  versus  $E_p$  (not published here), indicates only a moderate correlation ( $r^2$  0.77). An obvious reason for the breakdown in the correlation is the difference in time scale for these two types of oxidation experiments. The p.e.s. ionization is extremely rapid and the position of the first peak maximum ( $I_{p1}$ ) is the measure of the energy gap between neutral enamine and its cation radical of the same geometry as the neutral enamine. In contrast, the electrochemical experiment is far slower. Where the oxidation process is reversible the corresponding standard potential measures the energy gap between the neutral enamine and the relaxed form of its radical cation. However the oxidation is irreversible and the peak potential is influenced by electron transfer kinetics as well as by the thermodynamics of the oxidation process. Furthermore the electrochemical potentials are effected by solvation of the radical cations which may vary considerably in the homologous series of enamines. The situation may be compared with ionization in hydrazines.<sup>15</sup>

*Conclusions.*—Our findings can be summarized as follows. (1) The oxidation process of the enamines is irreversible. The oxidation step (heterogeneous electron transfer) is rate determining. (2) The lifetimes of the intermediate cation radicals are <0.2 ms. A more accurate determination is limited by the experimental conditions. (3) The trends in the anodic peak

potentials are not in complete accord with the trends obtained from the ionization potentials. In the former pyrrolidine activates the double bond most strongly. The highest potentials are required for the oxidation of 1-methylpiperazino- and morpholino-enamines. In more detail the order of peak potentials as a function of the amine component is as follows:  $7,8 < 5 < 6 < 1\text{-MP} < \text{MO}$ . A variation in the ketone component hardly influences the peak potentials. Their trends are not significant.

On the other hand the lowest ionization potentials are observed for the enamines derived from hexa- and heptamethyleneimine. Here the order of ionization potentials is  $7, 8 < 5 < 6, 1\text{-MP} < \text{MO}$ . The moderate correlation between ionization potentials and anodic peak potentials is due to the nonadiabatic p.e.s. ionization experiments in comparison with the adiabatic formation of radical cations in the electrochemical oxidation.

## Experimental

*Preparation of Enamines.*—All enamines were synthesized according to Stork *et al.*<sup>16</sup> A solution of ketone (0.2 mol) and amine (0.25 mol) in toluene (60 ml) was refluxed using a water separator. Depending on the reactivity of the components the reaction time varied between 4 and 30 h. In some cases the water separation was very slow and therefore a small amount of toluenesulphonic acid was added. After the water separation had stopped the solvent was removed and the residue was distilled *in vacuo*. The enamines were characterized by <sup>1</sup>H n.m.r. and i.r. spectroscopy.

(2) *Electrochemical Measurements.*—(a) *Materials.* In all experiments acetonitrile was used as solvent. Acetonitrile (Merck Uvasol; water content maximum 0.03%) was dried over a column of Al<sub>2</sub>O<sub>3</sub> (ca. 300 g Al<sub>2</sub>O<sub>3</sub> per litre of solvent). Before use Al<sub>2</sub>O<sub>3</sub> was activated at 300–350 °C *in vacuo* over P<sub>2</sub>O<sub>5</sub> for ca. 10 h.<sup>17</sup> Tetrabutylammonium tetrafluoroborate was obtained from Fluka (purissimum) and dried *in vacuo* at 100 °C over P<sub>2</sub>O<sub>5</sub>.

(b) *Electrochemical apparatus.* The measurements were carried out with a Princeton Applied Research (PAR) model 173 potentiostat equipped with a PAR model 179 digital coulometer and a PAR model 175 universal programmer. The PAR model 179 digital coulometer provided a positive feedback compensation for ohmic drop between the working and the reference electrode. The results were recorded directly on a X–Y recorder or stored on a waveform recorder (Biomation model 805).

For cyclic voltammetry and chronoamperometry a cell with a three-electrode configuration similar to that of Van Duyne and Reilly<sup>17</sup> was used. The working electrode was a PAR gold disk electrode, the reference electrode a saturated calomel electrode (s.c.e.). The distance between the working electrode and the tip of the Haber–Luggin capillary probe was ca. 1 mm, to minimize the i.r. drop. If necessary, positive feedback compensation was applied. A platinum wire served as a counter electrode. Coulometry was carried out with a platinum gauze electrode.

All values of electrode potentials reported in this work refer to the s.c.e. The liquid junction potential between the aqueous reference electrode and the acetonitrile solution was assumed to be constant and not taken into consideration.<sup>18</sup>

(c) *Cyclic voltammetry.* All electrochemical measurements were carried out at 25 °C in acetonitrile solutions with 0.1M-tetrabutylammonium tetrafluoroborate as the supporting electrolyte. The gold disk was repeatedly polished with 0.5 μm alumina during each series of measurements. Before each measurement the solution was purged with dried argon in order to remove oxygen. The anodic peak potentials were always reproducible to within ± 20 mV.

(d) *Measurement of the diffusion coefficient.* The diffusion coefficients were determined by chronoamperometric *I*–*t* curves.<sup>19</sup> A potential step from 0 V to a value ca. 0.2 V more anodic than the corresponding cyclic voltammetric peak potential was applied to the working electrode in order to establish diffusion control of the electron transfer. The decay of the current with time is given by the Cottrell equation (7). In

$$I = \frac{nFAcD^{\frac{1}{2}}}{(\pi t)^{\frac{1}{2}}} \quad (7)$$

case of undisturbed linear diffusion the product *I**t*<sup>½</sup> should be constant. For the enamines it was constant for only ca. 5 s. A typical example for the measurements is given for 1-MP/8; the product *I**t*<sup>½</sup> is 27.77 ± 0.01 μA s<sup>½</sup>.

The diffusion coefficients *D* were determined from (a) plots of *I**t*<sup>½</sup> versus *t* and extrapolation to *I**t*<sup>½</sup> (at zero atime) and from the slopes of the plots of *I* versus *t*<sup>–½</sup>.<sup>19</sup> Both sets of values are in perfect agreement with each other. Table 4 summarizes the diffusion coefficients of all enamines. They differ only slightly and no dependence of the diffusion coefficient on the structures of the enamines is apparent.

The area of the working electrode required for the evaluation of equation (7) was calibrated with ferrocene. The diffusion coefficient of ferrocene is *D* 2.4.10<sup>–5</sup> cm<sup>2</sup> s<sup>–1</sup>.<sup>19</sup> The area of the gold disk electrode was 0.095 cm<sup>2</sup>.

(e) *Lifetime of the cation radicals.* Enamine solutions (ca. 10<sup>–3</sup>M) in acetonitrile—0.1M-Bu<sub>4</sub>NBF<sub>4</sub> were investigated by double potential step chronoamperometry at 25 °C.<sup>20</sup> First for a time period τ the potential applied to the working electrode was set from 0 V to a value ca. 0.2 V more anodic than the corresponding cyclic voltammetric peak potential. Next the potential was returned to 0 V for an equal time period τ. The current–time response of the first step represented a sharp anodic current maximum (half-life ca. 80 μs) due to the charging of the double layer of the electrode followed by a faradaic anodic current. The latter was caused by the oxidation of the enamines and decayed with the square root of time. Even for a time period τ as short as 0.2 ms the current–time curve of the second step revealed only the cathodic current maximum of the charging current. This is indicated by a comparison with the pure charging current obtained by the same experiment, but in absence of the enamine. No faradaic current due to the reduction of the cation radicals which were produced in the first (oxidation) step could be observed. This was tested and proven for all enamines. Current–time responses of time periods τ shorter than 0.2 ms were not evaluated, because of the half-life of the charging current maximum. At 0.2 ms the faradaic component of the total current was still ca. 70% but only ca. 15% at the half-life of the charging current maximum. Hence this method establishes an upper limit of 0.2 ms for the lifetime of the enamine cation radical.

(f) *Coulometry.* In order to determine the number of electrons involved in the oxidation process we performed potential-controlled electrolysis at a platinum gauze electrode. The applied potential was set to the cyclic voltammetric peak potential of the enamine. The concentration of the enamine was ca. 5.10<sup>–5</sup>M in acetonitrile containing 0.1M-tetrabutylammonium tetrafluoroborate as supporting electrolyte. The total amount of charge afforded for the exhaustive electrolysis was counted by the PAR model 179 digital coulometer.

For some representative enamines Table 5 summarizes the applied potentials and the number *n* of electrons afforded per enamine molecule. The data reveal that only one electron is transferred in the oxidation process.

(3) *Measurements of the Ionization Potentials.*—The photoelectron spectra of all enamines were recorded with a UPG 200

**Table 4.** Diffusion coefficients  $D$  (in  $10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ) of all enamines. A refers to the amine component and K to the ketone component

	A						
	5	6	1-MP	MO	7	8	
K	5	1.5	1.6	2.0	1.8	0.9	0.7
	6	1.3	2.3	2.0	1.5	1.6	1.6
	7	1.2	1.9	2.0	1.5	1.5	1.4
	8	1.2	2.2	1.7	2.3	1.3	1.8

**Table 5.** Applied potentials  $E/V$  and number of electrons  $n$  afforded in the coulometric experiments

Enamine	$E/V$	$n$
MO/6	0.65	1.06
1-MP/7	0.65	0.91
6/8	0.5	1.06
8/8	0.45	0.98

spectrometer (Leybold-Heraeus) with  $\text{He}^I$  excitation (21.21 eV). The calibration of the energy scale was performed with an Ar-Xe mixture. The accuracy of the measurements was  $\pm 0.05$  eV for the bands.

### Acknowledgements

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