USE OF CURRENT-LESS POTENTIAL–TIME CURVES FOR DETERMINING THE RATE CONSTANTS OF AZO COPULATION REACTIONS

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The method of current-less potential–time curves was applied to the determination of rate constants for five azo copulation reactions, where the dyes formed need not be soluble in the reaction medium. The results are compared with those from the literature.

It has been shown in our preceding work[1] that reactions of other than redox type, *e.g.* copulation, can be studied by the method of current-less *E–t* curves. Previous authors studying the kinetics of the formation of soluble azo compounds used spectrophotometry to indicate the dye formation[2–30] or the consumption of the diazo compound[31], which was sometimes indicated amperometrically[32,33]. Reactions yielding insoluble azo dyes have been studied to a small extent[34]. It is known that the reaction between diazonium ions and a passive component is of the second order. The precipitate formed hinders the use of the mentioned methods; however, in the method of current-less *E–t* curves using a ground gold indicator electrode the presence of a suspension does not interfere since the electrode surface is constantly renewed.

The present work deals with the determination of rate constants of azo copulation reactions leading to the formation of either soluble or insoluble azo dyes.

EXPERIMENTAL

Chemicals

Aniline-4-sulphonic acid of reagent grade (Fluka, Switzerland), disodium salt of 1,8-dihydroxynaphthalene-3,6-disulphonic acid of reagent grade (Loba-Chemie, Austria), and 2-hydroxynaphthalene-6-sulphonic acid pure (VCHZ Synthesia, Pardubice-Semtín, ČSSR) were doubly recrystallized from hot water and filtered through active carbon. *p*-Cresol of reagent grade (Spolek pro chemickou a hutní výrobu, Ústí n. Labem, ČSSR). *p*-Aminoacetanilide of technical grade (same manufacturer) was doubly recrystallized from ethanol and filtered through active carbon. N,N-dihydroxyethyl-*m*-toluidine pure (DIHEMT) was recrystallized from ethanol and filtered through active carbon. Methyl ester of *p*-aminobenzoic acid and 1-phenyl-3-methyl-5-pyrazolon were doubly recrystallized from ethanol and filtered through active carbon. The purity of the mentioned chemicals was checked by elementary analysis.

The following detergents were used. Synferol EH (VÚOS Pardubice-Rybitví), amino active detergent based on sulphonated organic residue, dodecylbenzenesulphonic acid, denoted as NANZA sulpho acid (Spolek pro chemickou a hutní výrobu, Ústí n. Labem), and Slovaton O 25%, in substance oxethylated alcohols C_{12}—C_{18} (Chemické závody W. Piecka, Nováky, ČSSR).

Other chemicals were melted sodium acetate, acetic acid, hydrochloric acid, urea, potassium chloride, sodium nitrite, sodium hydrogen phosphate, citric acid, sodium hydroxide, boric acid, calcinated sodium carbonate, all of reagent grade from Lachema Brno, ČSSR, and sodium tetraborate of reagent grade from Spolana Neratovice, ČSSR. Buffer solutions of pH 3, 4, 4·5, 5, 5·6, 6, 9, 9·5, 10, 10·5, and 11 of unit ionic strength were prepared according to tabulated recipes[35].

Preparation of Diazonium Salts

A stock solution of 0·025M aniline-4-sulphonic acid in 0·5M-HCl was kept at 0—5°C. For diazotation, 25 ml of this solution was mixed with 0·5 ml of concentrated HCl and about 1·5 fold excess of $NaNO_2$. After about 20 min. the excess of nitrite (checked by iodide-starch paper) was decomposed by adding an excess of solid urea. Solutions of 0·01 and 0·025M diazotated *p*-nitroaniline and 0·05M diazotated methyl ester of *p*-aminobenzoic acid were prepared and stored in the same way. No change in colour of the solutions or in the rate constant was observed after 48 h of storage. For diazotation of *p*-aminoacetanilide, a 0·1M stock solution in 0·1M-HCl was prepared, cooled down to 0—5°C, and 25 ml of this solution was mixed with 1 ml of concentrated HCl. Further procedure was the same as above. A solution of *p*-aminoacetanilide in more concentrated HCl cannot be prepared since it hydrolyses partially to *p*-phenylenediamine and NO_2^- ions have an oxidising effect.

Preparation of Solutions of Passive Components

A 0·05M stock solution of 1,8-dihydroxynaphthalene-3,6-disulphonic acid was prepared in distilled water. A stock solution of 0·1M *p*-cresol in distilled water was prepared with an addition of 5 wt.% of NANZA acid; 0·025M 2-hydroxynaphthalene-6-sulphonic acid was prepared in distilled water; 0·05M 1-phenyl-3-methyl-5-pyrazolone with 3 wt.% of Slovaton O 25% was dissolved in distilled water; and 0·01M N,N-dihydroxyethyl-*m*-toluidine in distilled water was prepared either without or with 0·4 wt.% Synferol EH.

Apparatus

Potential-time curves were recorded on an apparatus described previously[36]. A ground gold rotating electrode[37] served as indicator electrode. Similar electrodes of other materials (Pt, C) were inactive with respect to concentration change of the diazonium salts.

RESULTS AND DISCUSSION

The following copulation reactions were chosen for the purpose of the present study.

I) Diazotated aniline-4-sulphonic acid with 1,8-dihydroxyanphthalene-3,6-disulphonic acid (homogeneous reaction).

II) Diazotated *p*-nitroaniline with 2-hydroxynaphthalene-6-sulphonic acid (precipitate formation at pH 5·6 and 25°C, but not immediately after mixing the components).

III) Diazotated *p*-nitroaniline with N,N-dihydroxyethyl-*m*-toluindie (emulsion formation) with or without the detergent Synferol EH. The product is a dispersed dye Ostacet red P2G denoted in Colour Index as Disperse red 17. The reaction kinetics has not been studied yet.

IV) Diazotated *p*-aminoacetanilide with *p*-cresol (precipitate formation). The data in Table I were obtained in the presence of the detergent Slovaton O. The product is an insoluble dye Ostacet yellow E–LR. The reaction kinetics has not been studied yet.

TABLE I

Rate constants of copulation reactions

Reaction	pH	t, °C	k, $dm^3 mol^{-1} s^{-1}$		k according to literature	
I	4	15	24·6 ± 1·49		26·56 ± 0·89[a] 37·47 ± 0·99[b]	30·99 ± 2·07[a] 25·75 ± 4·83[d]
I	4	25	39·29 ± 1·68		37·1 ± 0·4[a]	37·48 ± 0·38[b]
I	4	35	50·2 ± 4·4			
I	5	15	345·5 ± 29·7		330·9 ± 25·4[c]	302·1 ± 28·9[d]
I	5·6	15	886·2 ± 38·6		625·9 ± 77·9[c]	645·5 ± 74·9[d]
II	5·6	25	80·49 ± 4·03		77·85 ± 5·23 (ref.[34])	
III	4	15	281·2 ± 11·1[e]	258·9 ± 9·3[f]	—	
III	4	25	459·2 ± 11·5[e]	442·2 ± 26·9[f]	—	
III	4	35	740·6 ± 68·2[e]	793·5 ± 51·0[f]	—	
III	4	45	1 113·6 ± 215·1[e]	1 173·6 ± 154·2[f]	—	
IV	3	35	0·41 ± 0·06		—	
IV	3	45	9·76 ± 0·32		—	
IV	4	25	5·52 ± 0·13		—	
IV	4	35	35·53 ± 3·49		—	
IV	4	45	84·26 ± 4·24		—	
IV	4·5	15	30·13 ± 2·19		—	
IV	4·5	25	71·34 ± 3·28		—	
IV	4·5	35	306·59 ± 30·33		—	
V	9	45	1·49 ± 0·14		—	
V	9·5	35	1·75 ± 0·11		—	
V	10	25	0·89 ± 0·11		0·86 ± 0·19 (ref.[34])	
V	10	35	2·16 ± 0·09		—	
V	10·5	15	0·99 ± 0·08		—	
V	10·5	25	2·44 ± 0·18		—	

[a] Determined spectrophotometrically in a batch reactor[34]; [b] by enthalpiometry[34]; [c] by spectrophotometry in a batch reactor[39]; [d] by spectrophotometry in an injection reactor[39]; [e] measured in the presence of a detergent; [f] in the absence of a detergent.

V) Diazotated methyl ester of *p*-aminobenzoic acid with 1-phenyl-3-methyl--5-pyrazolone (precipitate formation) in the presence of NANZA acid. The product is an insoluble dye Ostacet yellow P2G.

The rate constants were determined from measured sets of *E–t* curves by plotting $t(1 - n)$ against ln n according to ref.[38]. The gold indicator electrode behaved ideally in the case of reaction(*I*) (soluble dye formation, $\Theta = 1$), but nonideally in other cases (pigment formation, $\Theta \neq 1$). The dependences of $t(1 - n)$ on ln n showed an extremum or an asymptote directed towards infinity as described in ref.[1]. The results are summarized, together with literature data, in Table I. Mean values were calculated from three or four results in good agreement with data from the literature[34,39].

It is apparent that the method of current-less *E–t* curves can be suitably employed in studying the kinetics of azo copulation reactions especially in cases where the dye formed is not soluble in the reaction medium. Thus it may be expected that the method will find application in dye chemistry.

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