

THE USE OF COPPER(III) COMPLEX COMPOUNDS FOR THE THERMOCHEMICAL ANALYSIS (DIE) OF DIFFERENT ORGANIC SUBSTANCES

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(Received November 18, 1985)

Potassium diperiodatocuprate(III), $K_7[Cu(IO_6)_2]$, was tested as a reagent for the determination of mono- and disaccharides by means of direct injection enthalpimetry. The reagent reacted readily with acyclic polyhydroxy compounds, the reaction proceeding the better, the more hydroxy groups there were in the substance and the closer the hydroxy groups were one to the other. It also reacted readily with phenols, the polyhydric ones in particular. Carbonyl and amino compounds mostly didn't react or did so slowly, but reacted readily in the presence of some other reactive group such as hydroxy, sulphhydryl or thioxo group. Semicarbazide reacted readily, presumably due to the presence of the reactive $-CO-NH-$ group. It is concluded that carboxy groups in the proximity of hydroxy groups exercise a positive effect on the reaction. The presence of a nitro or sulphonic acid group has a negative effect on the course of the reaction with the copper(III) compound.

For the direct determination of glucose, Beck [1] suggested the use of certain copper(III) complex compounds as titration reagents, for example potassium diperiodatocuprate(III), $K_7[Cu(IO_6)_2]$. However, in titrations of this kind it is difficult to determine the change in colour at the equivalence point.

In our assays conducted with the objective of using potentiometric titration with this reagent for the determination of different mono- and disaccharides, it was observed that the reaction occurred with sufficient rapidity only when the copper(III) compound was present in excess [2]. From this finding, it was concluded that the reaction is potentially of use for the determination of sugars by means of thermochemical analysis, actually by direct injection enthalpimetry (DIE): the reagent is added in excess and always in one portion to the solution under analysis, and the amount of heat evolved in the reaction indicates the quantity of the

substance to be determined, which is ascertained from the calibration curve, plotted by means of standards. The method was therefore tested for its applicability to the determination of sugars and other organic substances with copper(III) compounds.

Experimental

The solution of potassium diperiodatocuprate(III), $K_7[Cu(IO_6)_2]$, to be used as reagent was prepared following the procedure described by Jenšovský [3] and by Berka et al. [4]: 12.485 g copper sulphate pentahydrate is dissolved in 100 ml boiling water and 23.002 g potassium metaperiodate is added. A concentrated aqueous solution of 56 g potassium hydroxide is slowly added to the yellow-green suspension of cupric periodate, which is maintained boiling. A dark-green solution containing partially-dissolved cupric periodate is obtained, to which about 20 g solid potassium peroxydisulphate is added in small amounts. The solution turns brown and the remaining cupric periodate dissolves in it. The remaining peroxydisulphate decomposes during boiling for 30 min. After cooling, crystals of potassium sulphate deposit, the solution is decanted into a volumetric flask and water is added to make a volume of 500 ml. The result is a 0.1 mol l^{-1} solution of potassium diperiodatocuprate(III) containing 2 mol l^{-1} potassium hydroxide. When stored in a polythene bottle, the solution is satisfactorily stable for several weeks.

For analysis, 10 ml of the reagent was injected into 100 ml of solution containing $1-5 \cdot 10^{-5} \text{ mol}$ of the substance to be analysed and (similarly as for the reagent) 2 mol l^{-1} potassium hydroxide.

The measurement was made with an E 1 enthalpiograph, constructed according to the design of Brandštetr et al. [5, 6]. The Wheatstone bridge of the E 1 enthalpiograph was loaded with 300 mV. A line recorder of the EZ 7 type (manufacturer: Laboratorní přístroje, Prague) was used to record the curves, the full scale range being 0–1 mV and the chart speed 40 mm per min.

Results and discussion

The experimental result documented that both mono- and disaccharides react readily with the copper(III) compound even at normal temperature, and appreciable amounts of heat are evolved that are directly proportional to the quantity of sugar contained in the solution. The data relating to experiments with solutions of different sugars are shown in Fig. 1. As the individual mono- and disaccharides evolve unequal amounts of heat due to the reaction, it is necessary to

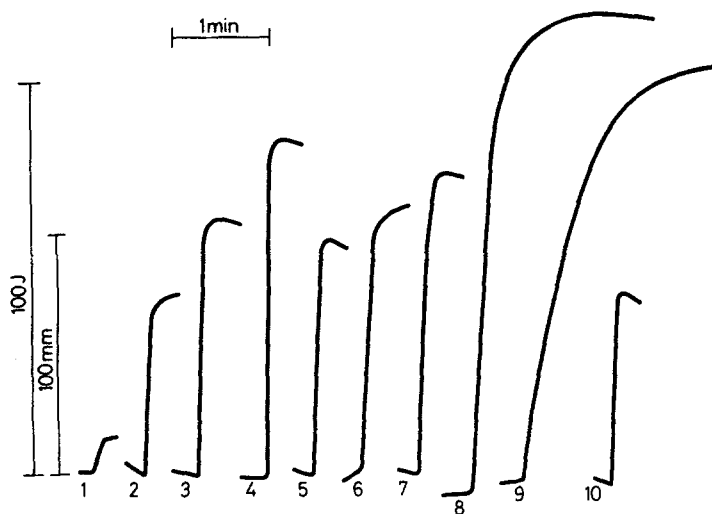


Fig. 1 Examples of enthalpimetric curves.

Alkaline solution of potassium doperiodatocuprate(III) in an amount of 10 ml, $c(\text{K}_7[\text{Cu}(\text{IO}_6)_2]) = 0.1 \text{ mol l}^{-1}$, $c(\text{KOH}) = 2 \text{ mol l}^{-1}$, was added to 100 ml solution of potassium hydroxide, $c(\text{KOH}) = 2 \text{ mol l}^{-1}$, containing $5 \cdot 10^{-5} \text{ mol}$ of the substance to be analysed, the addition being in one portion.

1 Ethylene glycol. – 2 Glycerol. – 3 Arabitol. – 4 Sorbitol. – 5 Arabinose. – 6 Fructose. – 7 Glucose. – 8 Maltose. – 9 Sucrose. – 10 Tartaric acid

plot special calibration curves for individual saccharides to evaluate the concentrations of individual mono- and disaccharides, as is usual with the quantitative analysis of sugars on the basis of their reaction with Fehling solution. In contrast to the quantitative analysis of sugars using Fehling solution, even the so-called non-reducing disaccharides react with the copper(III) compound, for instance sucrose and trahalose, which otherwise do not react with Fehling solution. It is true that the so-called non-reducing disaccharides react somewhat more slowly with the copper(III) salt than do the so-called reducing disaccharides, and monosaccharides in particular, but the height of the deviation can still be read with tolerable accuracy. There is another advantage of the new method over the traditional modes of determining sugars on the basis of the reaction with Fehling solution: the reaction of sugars with the copper(III) salt occurs immediately at laboratory temperature, whereas when sugars are reacted with Fehling solution, the solution must be heated first for a certain period of time.

The good results obtained in the thermochemical analysis of sugars using the copper(III) compound as reagent suggested to us the idea of testing the method with other organic substances.

As reported by Beck [7], the substances that are capable of forming chelate complexes with copper react most readily with copper(III) compounds, e.g.

polyhydroxy compounds the hydroxy groups of which are located in *o*-positions, α -amino acids, compounds containing —CO—NH— groups, and other substances.

To confirm the results of Beck's observations, we tested the reactions of different acyclic hydroxy compounds with potassium doperiodatocuprate(III). Our experimental results revealed that monohydric alcohols either did not react at all, or the reaction proceeded at a very low rate. In contrast, the dihydric alcohol ethylene glycol reacted readily with the copper(III) compound so that it was possible to read the height of the deviation. It therefore follows that this reaction is utilizable for the determination of ethylene glycol. The reaction of the trihydric alcohol glycerol was even faster, and it was accompanied by the liberation of an appreciably larger amount of heat. A comparison of the behaviours of different polyhydric alcohols and sugars suggested that the amount of heat liberated due to the reaction between the polyhydric alcohol and the copper(III) compound was the greater, the larger the number of hydroxy groups in the substance and the closer these hydroxy groups were to one another. Similarly, it was observed that either no reaction occurred between acyclic monohydroxy acids (malic and citric acids), and the copper(III) compound, or the rate of reaction was quite low (lactic acid), whereas tartaric acid (a dihydroxy acid) reacted quite readily with the copper(III) compound. The data relating to these experiments are shown in Fig. 1.

Further observations were concerned with the behaviour of phenols. The results revealed that monohydric phenols reacted much more readily with the copper(III) compound than did monohydric acyclic alcohols, although the reaction was a little slower (Fig. 2). The reactions of 1-naphthol and 2-naphthol with the copper(III) compound proceeded even more readily than did that of phenol. Polyhydric phenols reacted much more readily with copper(III) compounds than did monohydric phenols, and the amount of heat evolved in the reaction was appreciably larger too (for example pyrocatechol, hydroquinone, pyrogallol and phloroglucinol). In some of the polyhydric phenols under study, for example pyrocatechol, hydroquinone and pyrogallol, the different measurements furnished rather unequal deviation heights. It may be suggested that, in this particular case, the differences were due to the appreciable instability of the three phenols in alkaline solution with respect to atmospheric oxygen.

Phenolcarboxylic acids, similarly to phenols, reacted with potassium doperiodatocuprate(III), for example salicylic acid, acetylsalicylic acid and gallic acid. It will be evident from a comparison of the deviation heights measured for phenol and salicylic acid, for pyrogallol and gallic acid, and in particular for ethylene glycol and tartaric acid, that the presence of the carboxy group in the proximity of the hydroxy group had a positive effect on the reaction between the given compound and the copper(III) compound used (Figs 1 and 2).

In contrast, the presence of a nitro group or a sulphonic acid group in the

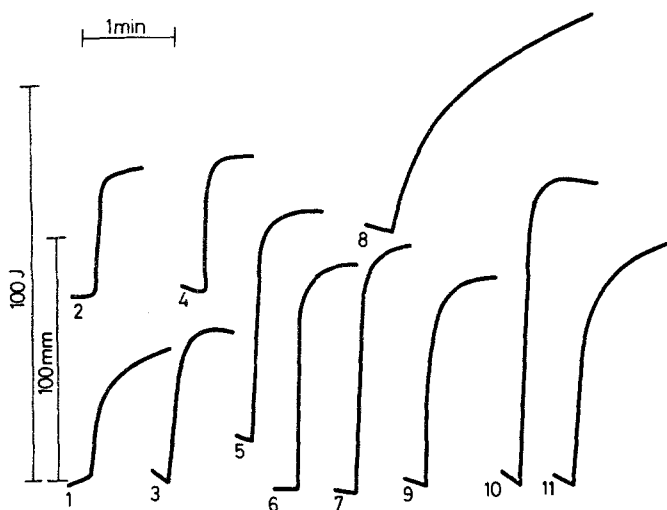


Fig. 2 Examples of enthalpimetric curves.

Alkaline solution of potassium doperiodatocuprate(III) in an amount of 10 ml, $c(\text{K}_7[\text{Cu}(\text{IO}_6)_2]) = 0.1 \text{ mol l}^{-1}$, $c(\text{KOH}) = 2 \text{ mol l}^{-1}$, was added to 100 ml solution of potassium hydroxide, $c(\text{KOH}) = 2 \text{ mol l}^{-1}$, containing $5 \cdot 10^{-5} \text{ mol}$ of the substance being analysed, the addition being in one portion.

1 Phenol. – 2 1-Naphthol. – 3 Smlicylic acid. – 4 Pyrocatechol. – 5 Hydroquinone. – 6 Pyrogallol. – 7 Gallic acid. – 8 Acetone. – 9 *p*-Benzoquinone. – 10 Alizarine. – 11 Sodium alizarine sulphonate

aromatic cycle had a negative effect on the reaction of the given substance with the copper(III) compound. Thus, while phenol and salicylic acid reacted readily with the copper(III) compound, both nitro derivatives and sulphonic acid derivatives of these compounds, such as *p*-nitrophenol, picric acid and sulphosalicylic acid, did not react at all.

Further observations were made on the reaction of substances containing the carbonyl group with the copper(III) compound (Fig. 2). The following results were obtained: formaldehyde did not react at all, acetone did so but at a rather low rate, and *p*-benzoquinone (containing two carbonyl groups) reacted readily. Both alizarin and quinalizarin, which, in addition to the two carbonyl groups, contain still more hydroxy groups, reacted quite readily and the reactions were accompanied by the liberation of appreciable amounts of heat. Sodium alizarin sulphonate reacted more slowly than alizarin, with liberation of a smaller amount of heat; nevertheless, it was possible to read the deviation quite well. In this instance, the hindering effect of the sulphonic acid group on the reaction with the copper(III) compound was manifested too.

Different amino compounds were also studied as concerns their reaction with

potassium diperiodatocuprate(III) (Fig. 3). The results may be summarized as follows: simple acyclic α -amino acids (with the exception of glycine, the reaction of which was relatively ready) either did not react at all or reacted at a very low rate and not readily, e.g. aspartic acid (Fig. 3). Only when some other reactive group was present in the α -amino acid under study, for example the hydroxy group in serine and threonine, the sulphhydryl group in cysteine, or the nitrogen heterocycle in tryptophan and histidine, did these α -amino acids show distinct deviations on reacting with the copper(III) compound (Fig. 3).

Of the amines under study, aniline and *o*-phenylenediamine reacted with the copper(III) compound, whereas *p*-phenylenediamine did not. Sulphanilic acid reacted more slowly than aniline with the copper(III) compound, and the amount of heat liberated was smaller (Fig. 3), which could again be explained as due to the presence of the sulphonic acid group.

Of the amides under test, acetamide, urea and its imide guanidine did not react with potassium diperiodatocuprate(III). On the other hand, the sulphur derivatives of these amides (thioacetamide and thiourea) (Fig. 3) gave very distinct deviations on reacting with the copper(III) compound, which indicated the reactivity of the thioxo group $\text{>C}=\text{S}$, as did semicarbazide (Fig. 3), presumably due to the reactive $-\text{CO}-\text{NH}-$ group present [8, 9].

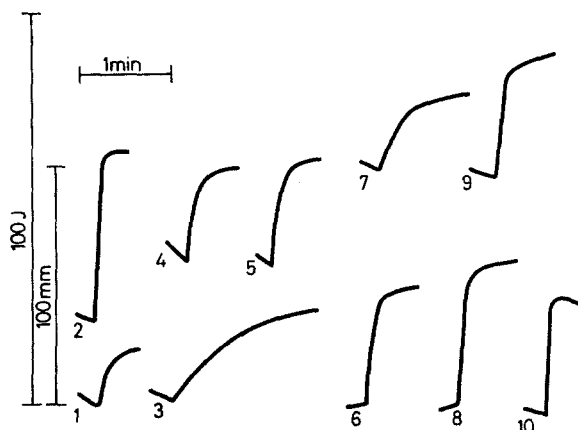


Fig. 3 Examples of enthalpimetric curves.

Alkaline solution of potassium diperiodatocuprate(III) in an amount of 10 ml $c(\text{K}_2[\text{Cu}(\text{IO}_6)_2]) = 0.1 \text{ ml l}^{-1}$, $c(\text{KOH}) = 2 \text{ mol l}^{-1}$, was added to 100 ml solution of potassium hydroxide, $c(\text{KOH}) = 2 \text{ mol l}^{-1}$, containing $5 \cdot 10^{-5} \text{ mol}$ of the substance being analysed, the addition being in one portion.

1 Glycine. - 2 Serine. - 3 Aspartic acid. - 4 Cysteine. - 5 Tryptophan. - 6 Aniline. - 7 Sulphanilic acid. - 8 Thioacetamide. - 9 Thiourea. - 10 Semicarbazide

Table 1 Measured deviations and calculated values of enthalpy changes in the reaction of different substances with potassium diperiodocuprate(III) 100 ml of the solution to be analysed contained always $5 \cdot 10^{-5}$ mol of respective compound

Analysed substance	*Average deviation, mm	Enthalpy change, ΔH , MJ/mol	Analysed substance	*Average deviation, mm	Enthalpy change, ΔH , MJ/mol
Ethylene glycol	17.0	0.21	Phloroglucinol	66.0	0.81
Glycerol	78.0	0.95	8-Hydroxyquinoline	54.0	0.66
Tartaric acid	85.0	1.04	8-Acetoxyquinoline	74.0	0.90
Arabitol	104.0	1.27	<i>p</i> -Benzoquinone	84.5	1.03
Mannitol	130.0	1.59	Alizarine	128.5	1.57
Sorbitol	138.6	1.69	Sodium alizarine sulphonate	69.5	0.85
Dulcitol	139.6	1.71	Quinalizarine	143.0	1.75
Rhamnose	91.5	1.11	Glycine	24.0	0.29
Xylose	95.6	1.12	Serine	75.0	0.92
Ribosc	113.4	1.39	Threonine	73.0	0.89
Arabinose	101.8	1.24	Cysteine	38.0	0.46
Sorbose	101.6	1.24	Tryptophan	42.0	0.51
Fructose	104.4	1.28	Asparagine	96.0	1.17
Glucose	126.0	1.54	Histidine	51.0	0.62
Mannose	124.2	1.51	Proline	30.0	0.37
Galactose	127.2	1.55	Tyrosine	73.0	0.89
Lactose	187.8	2.30	Aniline	48.0	0.59
Cellobiose	185.6	2.28	Acetaniide	28.0	0.34
Sucrose	176.2	2.16	Sulphanilic acid	30.0	0.37
Maltose	199.0	2.43	Sulphamamide	32.0	0.39
1-Naphitol	29.0	0.35	<i>o</i> -Phenylendiamine	23.0	0.28
2-Naphitol	50.0	0.61	Semicarbazide	53.0	0.69
<i>o</i> -Aminophenol	59.0	0.72	Thiourea	42.5	0.52
Salicylic acid	66.0	0.81	Thioacetamide	55.0	0.67
Acetyl-salicylic acid	63.0	0.77	Potassium xanthogenate	141.6	1.73

* Calculated from 3-5 parallel data.

A more detailed description of the results obtained in the testing of further organic substances for their reaction with potassium diperiodatocuprate(III) using direct injection enthalpimetry can be found in [10].

A comparison with the neutralization of hydrochloric acid with potassium hydroxide, of known neutralization heat, enabled us to calculate approximate values for the changes in enthalpy, ΔH , accompanying the reactions of different compounds with potassium diperiodatocuprate(III) used in excess under the conditions specified above. The values found for the changes in enthalpy, ΔH , are shown in Table 1. The appreciable amounts of heat liberated in the reactions indicate that the sensitivity of the reactions described here is sufficient.

Repeated measurements suggested that a relative standard deviation of about 1% is to be considered for the individual measurements, as is usual with this method.

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Zusammenfassung — Kalium-diperiodatocuprat(III), $K_7[Cu(JO_6)_2]$, wird als Reagenz für die Bestimmung von Mono- und Disacchariden durch direkte Injektionsenthalpimetrie vorgeschlagen. Es wurde festgestellt, daß das Reagenz leicht mit azyklischen Polyhydroxy-Verbindungen reagiert, und zwar umso besser, je mehr Hydroxylgruppen die Substanz enthält und je näher diese beieinander liegen. Das Reagenz reagiert leicht mit Phenolen, insbesondere wenn diese mehrere Hydroxylgruppen enthalten. Carbonyl- und Aminoverbindungen reagieren meistens nicht oder nur langsam, aber leicht in Gegenwart einiger anderer reaktiver Gruppen, wie Hydroxy-, Sulfhydryl- oder Thioxogruppen. Semicarbazid reagiert leicht, wahrscheinlich wegen der reaktiven Gruppe $—CO—NH_2—$. Es wird der Schluß gezogen, daß Carboxylgruppen in der Nachbarschaft von Hydroxylgruppen eine positive Wirkung auf die Reaktion ausüben. Die Anwesenheit der Nitro- oder Sulfonsäuregruppe wirkt sich negativ auf den Verlauf der Reaktion mit Kupfer(III)-Verbindungen aus.

Резюме — Диперйодатокупрат калия — $K_7[Cu(Ю_6)_2]$ — был предложен в качестве реагента для определения моно- и дисахаридов методом прямой инъекционной энталпиметрии. Экспериментальные результаты показали, что реагент легко реагирует с ациклическими полиоксисоединениями. При этом реакция лучше протекает с соединениями, содержащими большее

число гидроксильных групп и с более близким расположением их одна к другой. Реагент легко реагирует с фенолами и, в особенности, с полифенолами. Карбонильные и аминосоединения не реагируют или же реагируют очень медленно. Однако эти же соединения, содержащие окси-, тиокси- или сульфгидрильные группы, легко вступают в реакцию с реагентом. Семикарбазид легко реагирует, что, повидимому, обусловлено наличием реакционноспособной группы —CO—NH—. Установлено, что карбоксильные группы, находящиеся в непосредственной близости к гидроксильным группам, способствуют реакции, тогда как нитро- или сульфогруппы оказывают противоположное влияние.