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Letter to the Editor

Further comments on the Iodide Iodate Reaction Method for characterising micromixing

1. Introduction

The Iodide Iodate Reaction Method is a reliable and easy to perform method for mixing parameter studies but not yet a quantitative method for the determination of absolute mixing times as stated recently for the case for microstructured mixers [1] and for stirred vessels in a short communication by Bourne [2] to this journal.

To overcome this, Bourne points out the need for a 'robust kinetic model' of the Dushman reaction (Eq. (1)), determined at reactant concentrations relevant to mixing studies and suggests the application of 'modern techniques' such as stopped-flow apparatuses.

$$5I^- + IO_3{}^- + 6H^+ = 3I_2 + 3H_2O \tag{1}$$

In order to follow Bourne's suggestions, severe challenges need to be overcome, which are discussed in this letter. Experimental evidence is given, suggesting that the reaction rate of the Dushman reaction is too fast even for the best commercially available stopped-flow apparatuses. Microstructured mixers such as Cyclone Type Mixers can provide better mixing results and are hence proposed to be part of an experimental solution in the future determination of the kinetics of the Dushman reaction at reactant concentration relevant to mixing studies.

2. Mixing problems

In order to determine the kinetics of chemical reactions, mixing must be sufficiently faster than the chemical reaction to be investigated. The Iodide Iodate Reaction Method itself can serve as preliminary test to investigate if mixing is sufficiently fast to investigate the kinetics of the Dushman reaction at the respective concentrations. If considerable amounts of iodine (or triiodide in case of an I^- surplus) are detected it can be concluded that the rate of the Dushman reaction is faster than mixing in the chosen mixing device. If the mixing process is faster than the Dushman reaction, the chemical selectivity is solely governed by the chemical kinetics of the Dushman reaction and the neutralisation reaction, and thus no detectable amounts of iodine (or triiodide) would be found.

In order to achieve the relevant final concentration for mixing studies in stirred vessels [3–5] and microstructured static mixers [1], solutions with concentrations given in Table 1 were mixed in a stopped-flow apparatus. The experimentally obtained iodine yields are compared to those achieved in a cyclone type mixer [6,7].

2.1. Applying the Iodide Iodate Reaction Method to a stopped-flow apparatus

Stopped-flow instruments are rapid mixing devices used to study the chemical kinetics of fast chemical reactions. For successful experiments no larger extent of reaction should occur within the dead time of the apparatus. The dead time is determined by the path length between the mixing unit, the point where the mixture encounters the UV beam, the diameter of the tubing and the measurement cell and the total volume flow applied. Furthermore, the chosen mixer must be capable of mixing sufficiently faster than the reaction process. The latter demand can be tested by applying the Iodide Iodate Reaction Method at the appropriate reactant concentrations.

Solutions with the concentrations listed in Table 1 were mixed in a stopped-flow apparatus (bio-logic SFM-400) with the highest total volume flows (16 mL/s) possible (in order to achieve the best mixing results possible and to minimise the dead time). The resulting mixtures were collected at the outlet and examined for their UV absorbances (bio-logic MOS-200) at a wavelength of 353 nm with a standard 1 cm Hellma quartz cuvette, except for 2SC, which was measured in a 1 mm cuvette. As a mixing device a 'Berger ball mixer' (bbm) and 'micro Berger ball mixer' (μbbm) have been used. The experimental results are given in Table 2.

The experimentally determined triiodide concentrations shows that the Dushman reaction occurs in competition to the neutralisation of $H_2BO_3{}^-$ during mixing. Since mixing is faster than the dead time of the apparatus (0.25 ms; determined by bio-logic with the reducing reaction of 2,6-dichlorophenol by ascorbic acid), it can be stated that the Dushman reaction occurs at a significant extent at the relevant concentrations within 0.25 ms. Most likely the reaction time is much faster than that. Since the experimentally determined absorbance values at 353 nm are significantly reduced switching from the bbm to the μbbm, it is substantiated that a mixing problem (i.e. mass transfer limitation) is encountered.

2.2. Applying the Iodide Iodate Reaction Method to a microstructured cyclone type mixer

For the application of the Iodide Iodate Reaction Method to a microstructured cylone type mixer, it was recently shown that applying the concentrations abbreviated 1SC and 2SC led to no detectable amounts of triiodide in the resulting mixtures [6,7]. Only when applying higher reactant concentrations (three time the standard concentration for static mixers at the IMVT; 3SC), with corresponding higher reaction rates, can triiodide be detected in the resulting mixtures. As no triiodide is found at lower reactant concentrations, the kinetics of the Dushman reaction might be investigated for mixing processes corresponding

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Table 1
Concentration in mol/L of solutions relevant to mixing studies

	Standard concentration for static mixers ‘1SC’	Twice the standard concentration for static mixers ‘2SC’	Vessel concentrations ‘VC’
Solution 1			
Sulfuric acid H_2SO_4	0.015	0.03	0.004
Solution 2			
Potassium iodide KI	0.016	0.032	0.0233
Potassium iodate KIO_3	0.003	0.006	0.00467
Sodium hydroxide NaOH	0.045	0.900	0.1818
Hydroboric acid H_3BO_3	0.045	0.900	0.3636

Table 2
Experimentally obtained absorbance values for the resulting mixtures with the respective reactant concentrations using different mixers in the stopped-flow setup

Concentrations (see above)	bbm	μbbm
2SC	2.0 A.U. (1 mm cuvette)	Not measured
1SC	3.0 A.U.	1.24 A.U.
VC	1.8 A.U.	1.07 A.U.

to those concentrations such as mixing processes in stirred vessels.

3. Spectroscopic/solubility problems

When the Dushman reaction is investigated without the competition of the neutralisation step (applying solution 2 without the NaOH/H_3BO_3 buffer), this results in very high final iodine concentrations (1.4×10^{-2} M), which exceed the solubility of iodine in water (1.3×10^{-3} M [8]) by a factor of approximately 10. In order to overcome the solubility problem, an excess of iodine might be added [9]. The I_3^- as a reaction product possesses a much higher solubility but also a much higher molar absorbance coefficient at the respective peak maximum (2550 m^2/mol for I_3^- vs. 73 m^2/mol for I_2 [10]). Therefore, a spectroscopic saturation is encountered at complete conversion of IO_3^-. Assuming the occurrence of optical saturation at an absorbance value of 3.5, an optical cuvette has a theoretical maximal thickness of approximately 0.2 mm for the concentrations relevant to mixing studies in stirred vessels. In all work employing the Dushman reaction in mixing studies or for the determination of its kinetics, UV spectroscopy has been solely utilized. For the above mentioned reasons, its application in the determination of kinetics of the Dushman reaction at concentrations relevant to mixing studies is highly challenging.

4. Conclusions

In a short communication to this journal, Bourne alluded to the strong need for the determination of the kinetics of the Dushman reaction at reactant concentrations relevant to mixing studies in order to develop the Iodide Iodate Reaction Method into a quantitative method. In order to meet this requirement, some challenges need to be tackled. Among those, solubility problems, spectroscopic problems, and mixing problems are discussed in this letter. Experimental evidence is given that suggests that mixing in the best commercially available stopped-flow devices is much slower than the rate of the Dushman reaction at reactant concentrations relevant to mixing studies. When applying the Iodide Iodate Reaction Method to a microstructured cyclone type mixer, no triiodide is found in the mixing product at the same reactant concentrations, suggesting that this device is suitable for the determination of the kinetics of the Dushman reaction at the relevant reactant concentrations.

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