Effect of acetone on the dynamics of temporal oscillations and waves in the ruthenium-catalyzed Belousov-Zhabotinsky reaction

Titikan Somboon,[a] Prapin Wilairat,[a] Stefan C. Müller[b] and On-Uma Kheowan[a*]

[a]Department of Chemistry, Faculty of Science, Mahidol University, Rama 6 Road, Bangkok 10400, Thailand. *Corresponding author e-mail: onuma.khe@mahidol.ac.th

[b]Institut für Experimentelle Physik, Otto-von-Guericke-Universität, Universitätsplatz 2, D-39106, Magdeburg, Germany.

EIS 1: Variation of the stirring rate

1.1 Objective

To investigate the effect of the stirring rate on the oscillatory dynamics of the ruthenium-catalyzed BZ reaction

1.2 Experimental method

The BZ solution was continuously stirred by using a magnetic stirrer with different stirring rates varied from 150 - 600 rpm. The experimental setup is shown in Fig. 1. The reaction chamber was closed by a cork. Inside the chamber, there is 50 ml of the BZ solution and 25 ml of air space above the BZ solution. By using this reaction chamber, the produced gases, such as Br_2, evaporating and accumulating above the BZ solution can partially dissolve in the solution. The temperature was kept constant at 25.0 ± 0.2°C by using a water jacket connected to a thermostat. The oscillations were followed with a bromide selective electrode and a Pt electrode connected to a pH meter.

1.3 Results and discussion

The concentration profiles of Br^- at different stirring rates are shown in Fig. 2. The maximum concentration of Br^- (the maximum amplitude in each concentration profile) increases with increasing stirring rate. We also found that the oscillation period T_{to} significantly grows with increasing stirring rate, as shown in Fig. 3. There is a linear relation between T_{to} (s) and the stirring rate (rpm) as follows: $T_{to} = 0.05 * \text{stirring rate} + 45.50$. The enhancement of the stirring rate increases the concentration of Br^-. As the amount of Br^- increases, the system takes a longer time to remove Br^- via the process A, and consequently the period is lengthened.

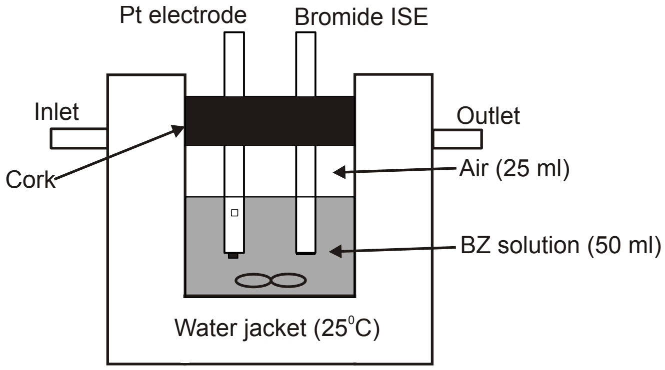

Fig. 1: Experimental setup for investigating the temporal oscillations.

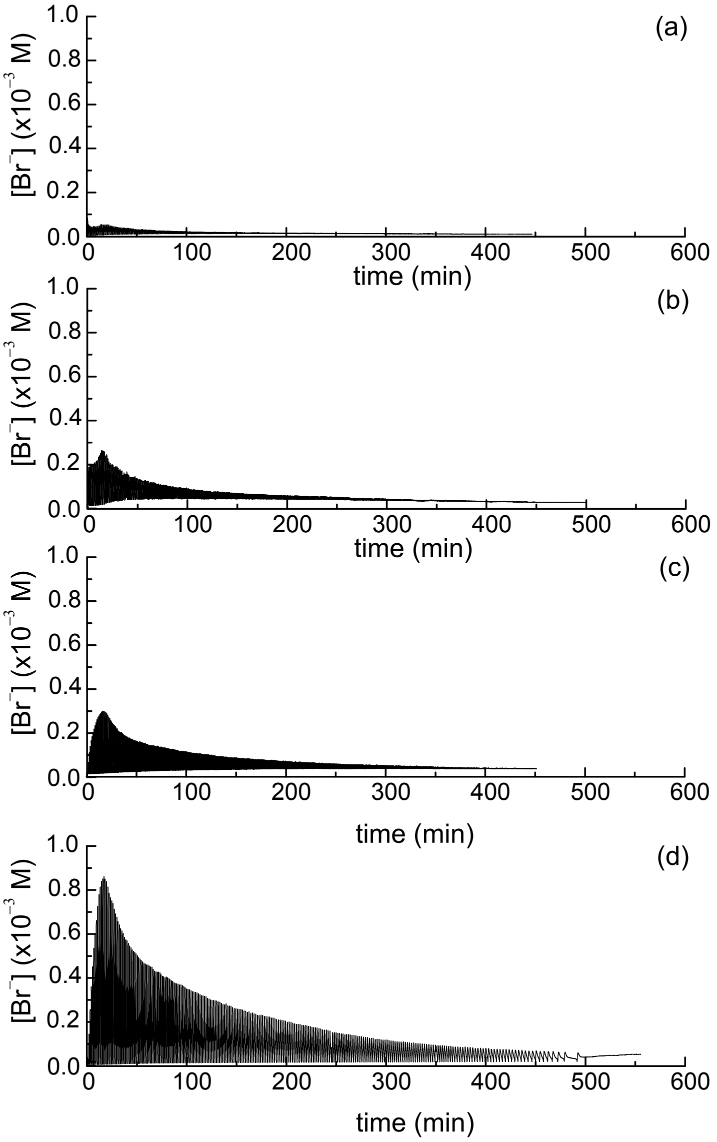

Fig. 2: Effect of the stirring rate on the concentration of Br^-. The stirring rate is (a) 150, (b) 300, (c) 450, and (d) 600 rpm. The recipe consisted of 0.05 M sodium bromate, 0.20 M malonic acid, 0.50 M sulfuric acid, 1.0 x 10^{-4} M tris (bipyridine) ruthenium (II) sulfate.

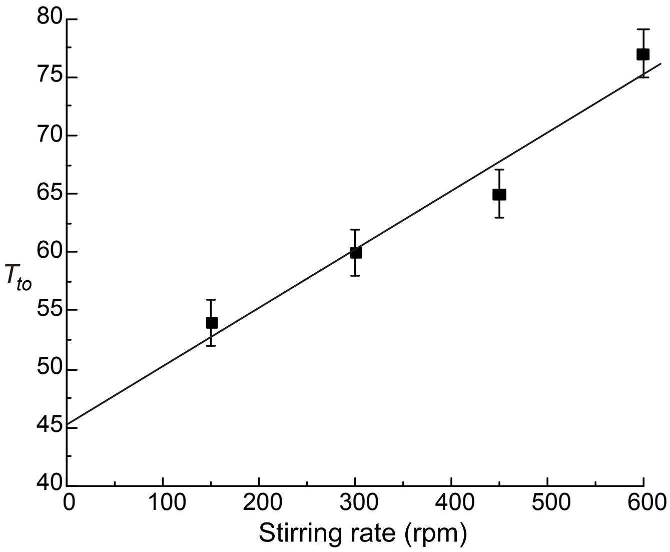

Fig. 3: Effect of the stirring rate on the oscillation period T_{to}. Each data point is averaged from 2 experiments.

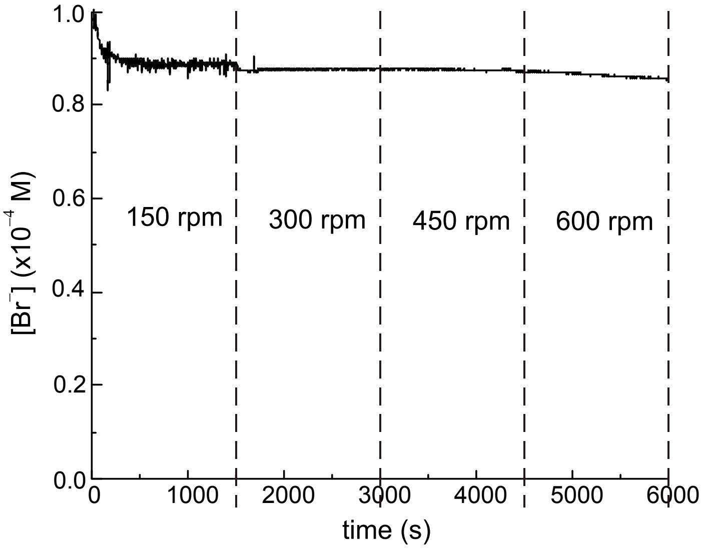

Fig. 4: No effect of stirring rate on the sensitivity of the bromide selective electrode. The solution with volume 50 ml is 1.0 x10^{-4} M of NaBr. The reaction chamber is closed and the temperature is 25.0 ± 0.2°C.

The sensitivity of the bromide ion selective electrode was investigated under different stirring rates. By using the constant concentration of 1.0 x10^{-4} M NaBr and varying the stirring rate, we found that the concentration of Br$^-$ remains constant for stirring rates up to 600 rpm, as shown in Fig. 4. This confirms that the increase of the stirring rate does not affect the sensitivity of the electrode. Therefore, the increase of the Br$^-$ concentration with increasing the stirring rate (Fig. 2) results from the dynamics of the BZ reaction.

EIS 2: Investigation of bromoacetone

2.1 Objective

To investigate bromoacetone in the BZ solution

2.2 Experimental method

The BZ solution with and without acetone was investigated. The solution consisted of 0.05 M $NaBrO_3$, 0.20 M malonic acid, 0.50 M H_2SO_4 and 0.05, 0.10, and 0.50 M acetone. Its volume was 10 ml. The reactants were mixed under constant stirring at a rate of 300 rpm for 5 min. Subsequently, bromoacetone was extracted by using dichloromethane. After that, it was investigated with a ^{1}H-NMR spectrometer (Bruker DPX-300) with solvent $CDCl_3$.

2.3 Results and discussion

The ^{1}H-NMR spectra for each concentration of acetone are shown in Figs. 5-8. The characteristic peaks of $BrCH_2COCH_3$ are at the positions of 3.90 (ppm, 2H) and 2.38 (ppm, 3H) [1]. For the BZ solution with 0.00 and 0.05 M acetone (Figs. 5 and 6), no characteristic peaks of $BrCH_2COCH_3$ are observed. However, characteristic peaks appear at 3.90 (ppm, 2H) and 2.38 (ppm, 3H) in cases of 0.10 and 0.50 M acetone, as shown in Figs. 7 and 8. In conclusion, $BrCH_2COCH_3$ is observed in the presence of acetone with initial concentrations of 0.10 and 0.50 M, whereas it is not observed under the condition of acetone concentrations of 0.00 and 0.05 M.

Reference:

1. Whitmore, F. C., Hollingshead, J. P. (1943), *Organic Syntheses*, 2, 88.

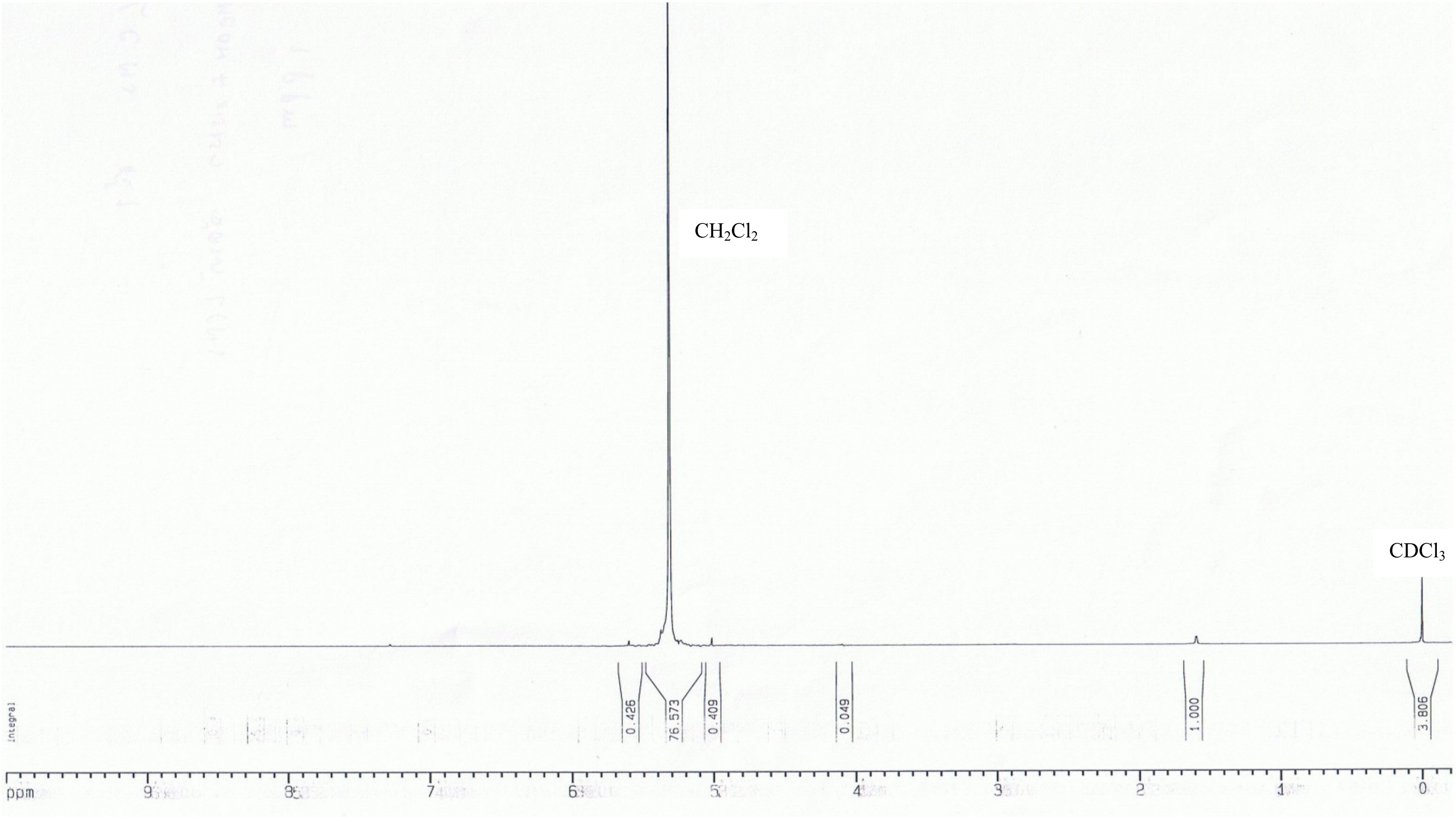

Fig. 5: ^{1}H-NMR spectrum of the BZ solution without acetone.

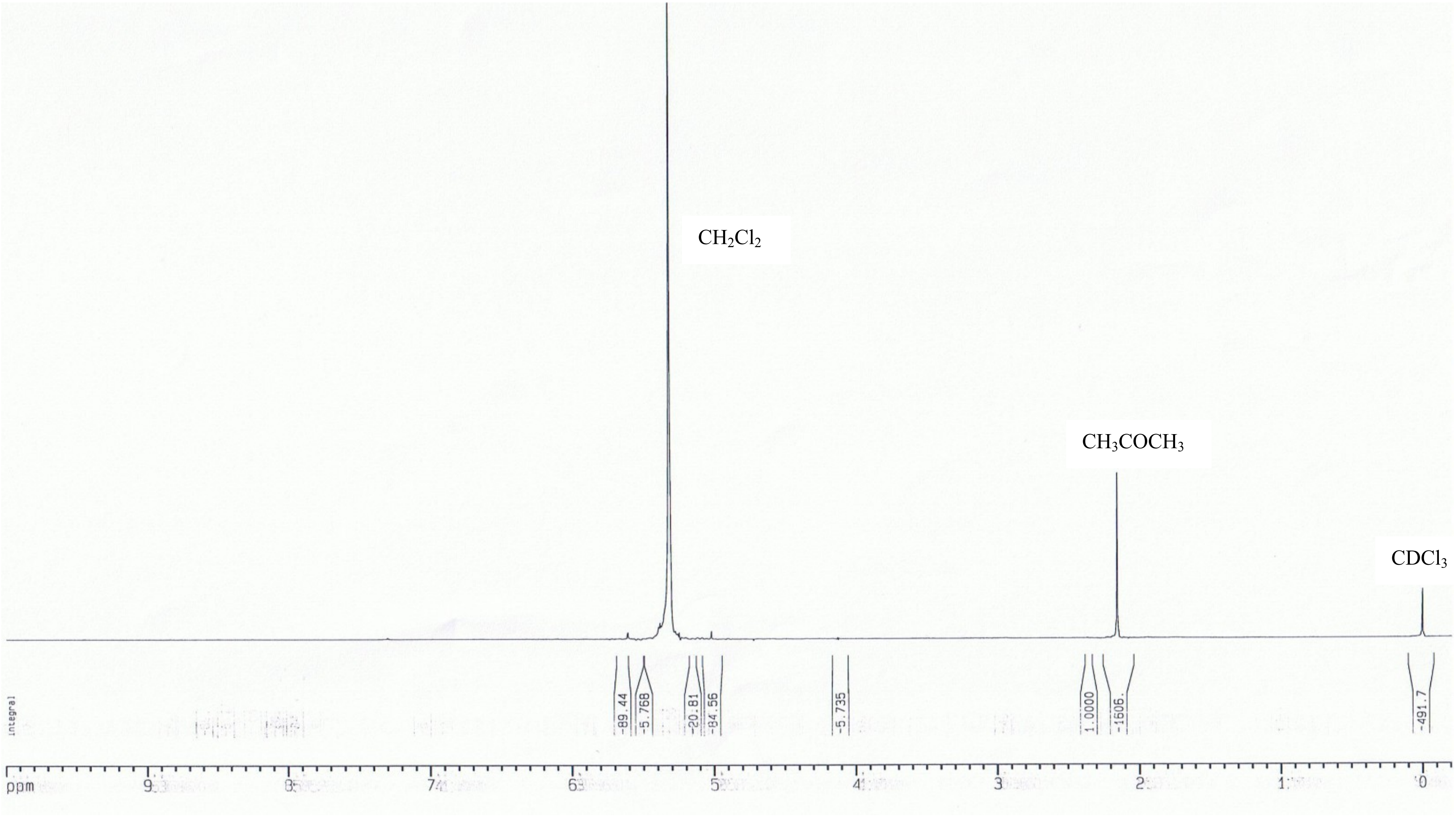

Fig. 6: ^{1}H-NMR spectrum of the BZ solution with 0.05 M acetone.

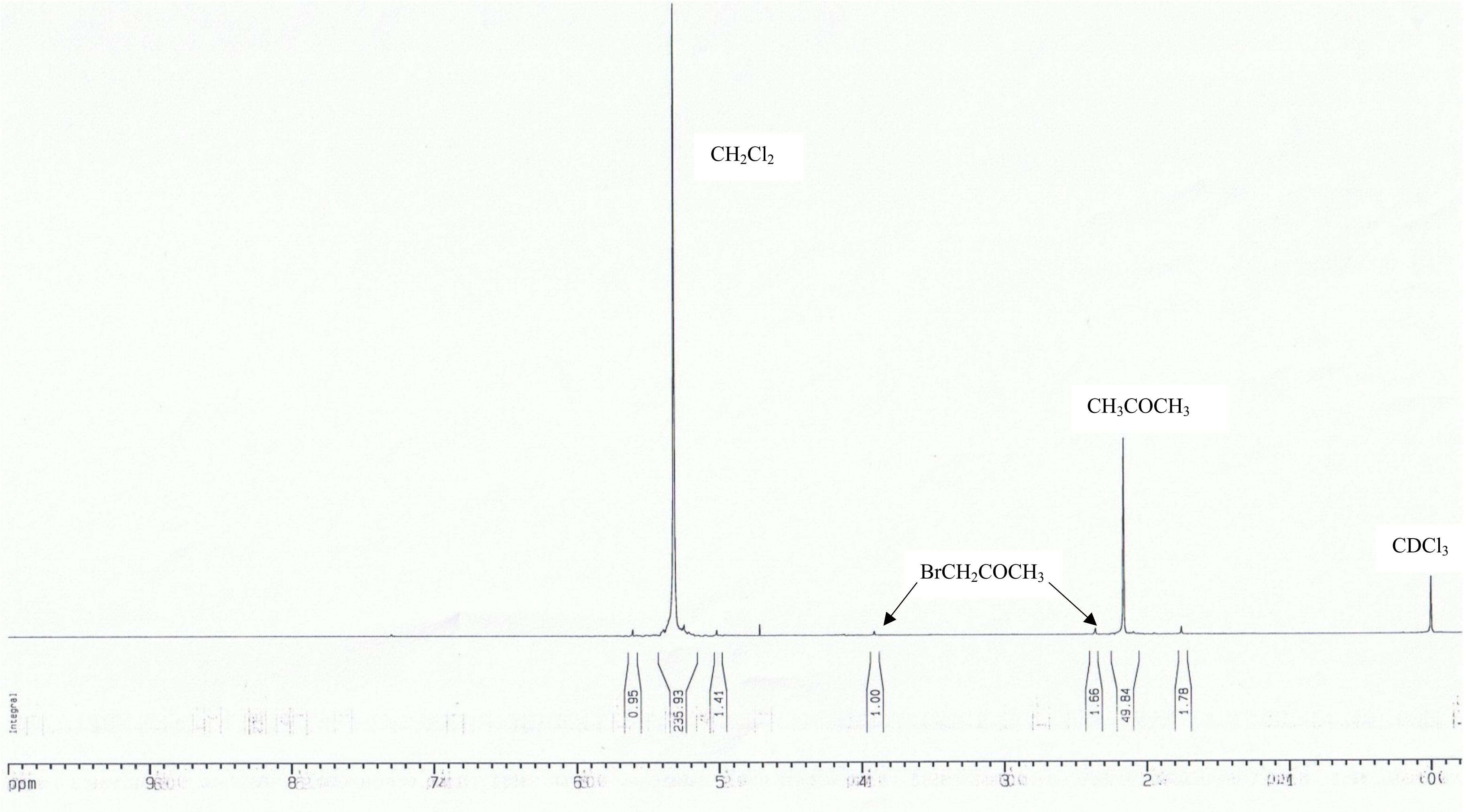

Fig. 7: ^{1}H-NMR spectrum of the BZ solution with 0.10 M acetone. Peaks of BrCH$_2$COCH$_3$ appear at 3.90 (ppm, 2H) and 2.38 (ppm, 3H).

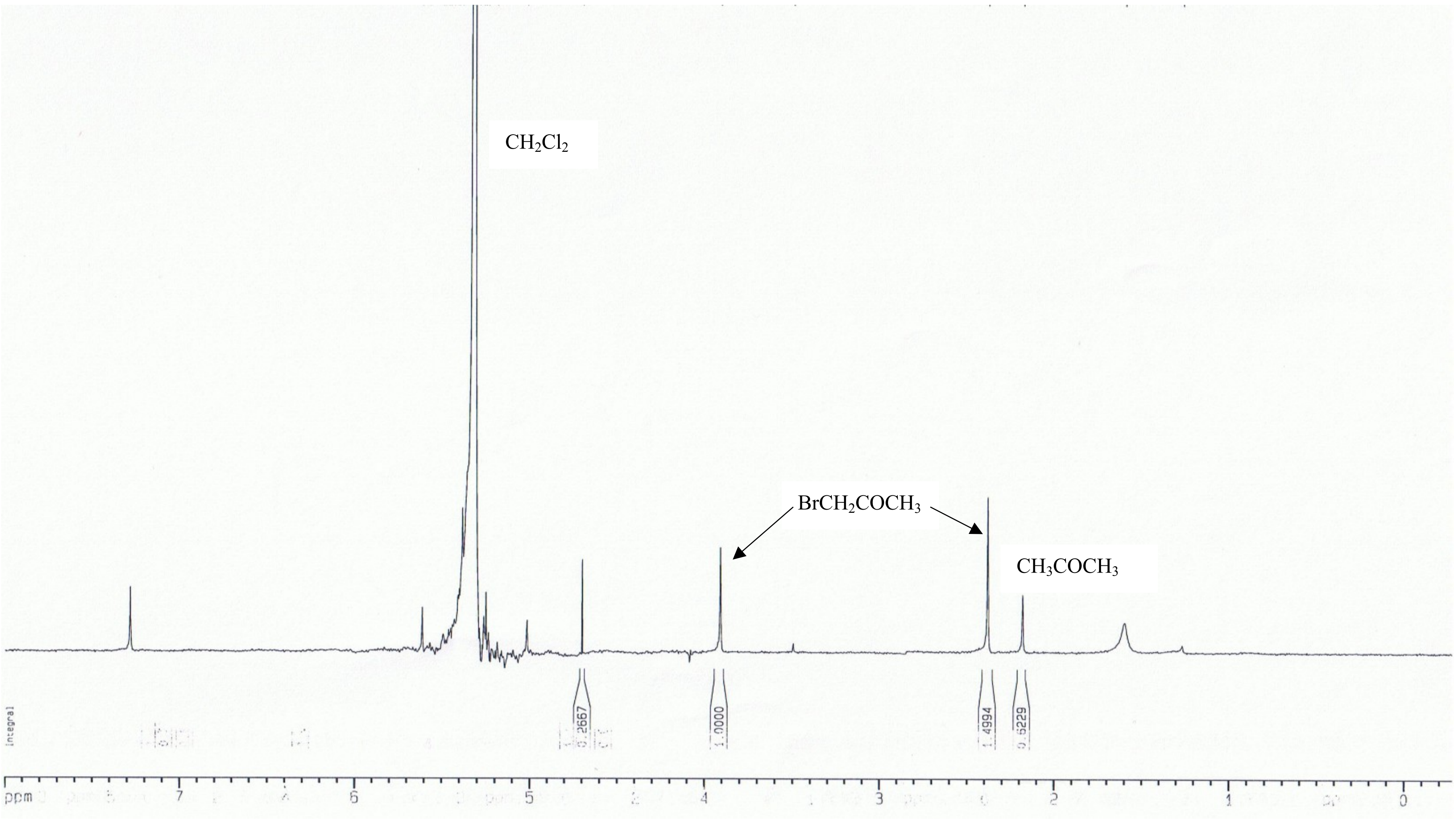

Fig. 8: ^{1}H-NMR spectrum of the BZ solution with 0.50 M acetone. Peaks of BrCH$_2$COCH$_3$ appear at 3.90 (ppm, 2H) and 2.38 (ppm, 3H).