



Mendeleev 2024

XIII International Conference on Chemistry
for Young Scientists

BOOK OF ABSTRACTS



St Petersburg
University

BOOK OF ABSTRACTS

**XIII International Conference on Chemistry
for Young Scientists “MENDELEEV 2024”**

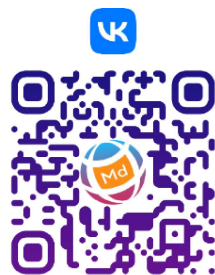
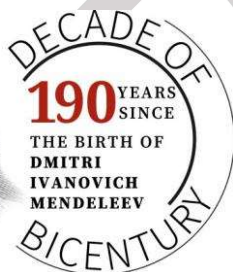
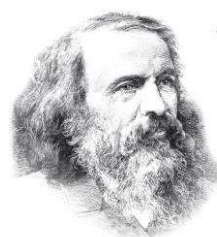
St Petersburg, Russia
September 2-6,
2024

ISBN 978-5-9651-1584-6

Book of abstracts contains theses of plenary, keynote, oral and poster presentations which were presented on **Mendeleev 2024**, the XIII International Conference on Chemistry for Young Scientists. The Mendeleev 2024 Conference hold in Saint Petersburg (September 6–10, 2024).

Abstracts presented in the original edition.

DEDICATED TO



@mendeleev.spbu



@Mendeleev_spbu

HALONIUM AND CHALCONIUM SALTS AS NONCOVALENT ORGANOCATALYSTS FOR ELECTROPHILIC ACTIVATION OF CARBONYL COMPOUNDS

Putnin I.O., Sysoeva A.A.

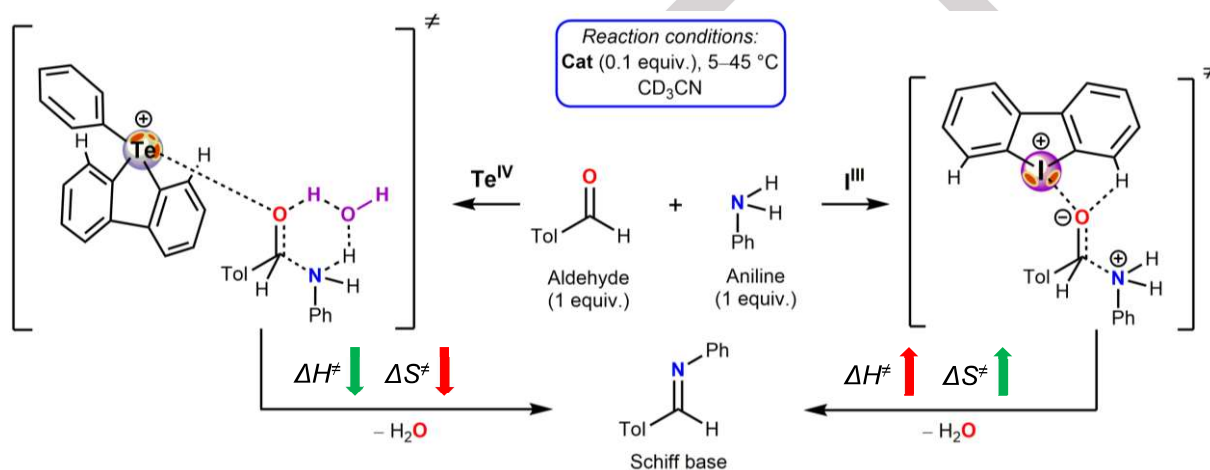
St. Petersburg State University, St. Petersburg, Russia

1st Year Master's Student

st117584@student.spbu.ru

Electrophilic activation of the carbonyl group is of great significance and widely used approach in modern organic synthesis. When classical Lewis acids such as metal-complex catalysts are used in these reactions, the metal electrophilically activates the carbonyl group making it a more convenient target for nucleophilic attack. Even though the entropy of activation (ΔS^\ddagger) of this reaction takes a more negative value due to the addition of the catalyst to the reaction substrate, the enthalpy of activation (ΔH^\ddagger) decreases more strongly due to the electrophilic activation of the carbonyl group, and therefore the reaction is accelerated.

In this study, we investigated the kinetics of the reaction of *para*-methylbenzaldehyde with aniline catalyzed by organic Lewis acids, namely telluronium (Te^{IV}) and idonium (I^{III}) salts. Based on the obtained activation parameters (ΔS^\ddagger , ΔH^\ddagger), plausible mechanisms of the model reaction involving Te^{IV} and I^{III} have been suggested (Scheme 1).



Scheme 1. Plausible mechanisms of the model reaction.

Based on the results of the conducted experiments, a number of thermodynamic and kinetic parameters of the reaction were calculated, including the ΔS^\ddagger values [$\text{kJ mol}^{-1} \text{K}^{-1}$] and ΔH^\ddagger [kJ mol^{-1}] for the non-catalyzed reaction [$-0.262(3)$; $19(1)$], for the reaction catalyzed by Te^{IV} [$-0.284(4)$; $8(1)$] and I^{III} [$-0.224(1)$; $22.9(1)$]. The kinetic data indicated that the catalytic effect of Te^{IV} is provided via decrease of ΔH^\ddagger of the reaction. This indicates a classical mechanism of electrophilic activation of the carbonyl group through the formation of a chalconium bond under additional coordination by a water molecule. The catalytic effect of I^{III} unexpectedly was caused by decrease of the ΔS^\ddagger absolute value. We assume that the reaction involving I^{III} proceeds through the formation of a zwitter-ionic transition state, the smaller stability and size of which increase ΔS^\ddagger and ΔH^\ddagger .

The data obtained on the kinetics of the model reaction make it possible to optimally select conditions for reactions involving carbonyl group catalyzed by chalconium and halonium salts. This study contributes to the theoretical understanding of mechanisms underlying electrophilic activation reactions.

Acknowledgements

This work was supported by the Russian Science Foundation (project No 23-73-10003; kinetic study) and Saint Petersburg State University (project No 103922061; synthetic work). Physicochemical studies were performed at the Center for Magnetic Resonance, Chemistry Educational Centre, and Center for Chemical Analysis and Materials Research (all at St. Petersburg State University).