Improving the Capture of CO2 by Substituted Monoethanolamines: Electronic Effects of Fluorine and Methyl Substituents

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CHEMPHYSCHEM
Volume: 13 Issue: 17 Pages: 3973-3980
DOI: 10.1002/cphc.201200471
Published: DEC 7 2012
View Journal Impact

Abstract

The influence of electronic and steric effects on the reaction between CO2 and monoethanolamine (MEA) absorbents is investigated using computational methods. The pKa of the alkanolamine, the reaction enthalpy for carbamate formation, and the hydrolytic carbamate stability are important factors for the efficiency of CO2 capture. The steric and electronic effects of CH3, CH2F, CHF2, CF3, F, dimethyl, difluoro, and bis(2-trifluoromethyl) substituents at the alpha carbon of MEA on this reaction are investigated. Density functional theory (DFT) (B3LYP, M06-2X, M08-HX and M11-L) and ab initio methods [spin component-scaled second-order Moller-Plesset theory (SCS-MP2), G3], each coupled with solvent models [conductor-like polarizable continuum model (CPCM) and universal solvation models (SM8 and SMD)], are shown to yield accurately calculated pKa values of the substituted MEAs. Specifically, G3, SCS-MP2, and M11-L methods coupled with the SMD and SM8 solvation models perform well with a mean unsigned error (MUE) of only 0.15, 0.24 and 0.25 pKa units, respectively. SCS-MP2 is used to calculate the reaction enthalpy for carbamate formation and the carbamate stability towards hydrolysis. With the introduction of beta-fluoro substituents (especially the CH2F moiety) the reaction enthalpy for the formation of carbamates can be fine-tuned to be less exothermic than that using the unsubstituted MEA. This implies a reduced energy requirement for the solvent-regeneration step in the post-combustion carbon-capture method, which is currently the energy-limiting step in efficient CO2 capture. beta-Fluoro-substituted MEAs are also shown to form less stable carbamates than MEA. Thus, beta-fluoro-substituted MEAs display a great potential for the use in the post-combustion carbon-capture process. Finally, a clear correlation is observed between the gas-phase basicity and the tendency to form carbamates. This allows for the rapid prediction of which species will be formed experimentally, and thus the CO2-absorbing capacities of alkanolamines can be estimated.

Keywords

Author Keywords: alkanolamines; basicity; carbamates; carbon dioxide fixation; computational chemistry

KeyWords Plus: MAIN-GROUP THERMOCHEMISTRY; FREE-ENERGY PERTURBATIONS; GAS-PHASE BASICITIES; AB-INITIO; NONCOVALENT INTERACTIONS; CARBON-DIOXIDE; AMINES; MOLECULES; ABSORPTION; ACCURACY

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Funding

Funding Agency	Grant Number
Dutch Ministry of Economic Affairs	

View funding text

Publisher

WILEY-V C H VERLAG GMBH, BOSCHSTRASSE 12, D-69469 WEINHEIM, GERMANY

Categories / Classification

Research Areas: Chemistry; Physics

Web of Science Categories: Chemistry, Physical; Physics, Atomic, Molecular & Chemical

Document Information

Document Type: Article

Language: English

Accession Number: WOS:000312038200032

PubMed ID: 22965750

ISSN: 1439-4235

Other Information

IDS Number: 050FJ

Cited References in Web of Science Core Collection: 48

Times Cited in Web of Science Core Collection: 17